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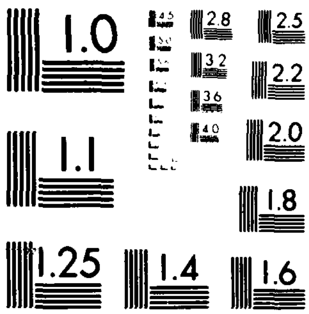
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LITHIUM-THIONYL CHLORIDE BATTERY

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We have delivered 100 D cells to the sponsor. The cell has also been tested for capacity retention after abusive storage at 72°C. We demonstrated the safety of the flat cylindrical cell during over discharge and voltage reversal at the 3.2A and 20A rates of the GLLD cell. We also studied the rate capability retention of the flat cell after storage.

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I. Introduction

The $Li/SOCl_2$ inorganic electrolyte system (1-4) is the highest energy density system known to date. It consists of a Li anode, a carbon cathode and $SOCl_2$, which acts both as a solvent and cathode active material. The electrolyte salt that has been used most extensively is $LiAlCl_4$, but salts such as $Li_2B_{10}Cl_{10}$ (5) and $Li_2O(AlCl_3)_2$ (6) have also been used successfully in this system for improving the shelf life characteristics.

The main objective of this program is to develop high rate $Li/SOCl_2$ cells and batteries for portable applications of the U. S. Army. The cells and batteries must deliver higher energy densities than are presently available and must be safe to handle under field conditions.

We carried out a detailed development (7) on the spirally wound D cell in order to establish their performance capabilities and to identify limitations in their performance and safety under various use and abuse conditions. Substantial progress was made in correction cell limitations. We found that spirally wound D cells approached the high rate requirements of the various U.S. Army applications more closely than do any other cell designs at the present time. We used this spirally wound D cell as a starting point and improved its rate capability to meet the requirements of two specific applications, namely the BA5590 battery for manpack radio and the battery for the GLLD Laser Designator.

We concentrated our effort on the development of the high rate spirally wound D cell during the first two quarters to determine whether it was possible for the D cell.to meet the performance requirements of the GLLD Laser Designator. The results obtained in the second quarter showed that the high rate D cells could deliver eighteen (18) bursts or 5.9 A.hr/cells compared to the three (3) bursts or 1A.hr/cell realized from the presently used Ni/Cd batteries. An advantage of the D cell over other cell geometries and configurations is that the D cell can be produced at our lithium battery manufacturing plant with only slight modifications of the existing process which is used for manufacturing spirally wound Li/SO_2 D cells. The results were encouraging and we are

continuing to improve the $Li/SOCl_2$ D cell so that it can meet a variety of high rate requirements, including the GLLD application.

During the third quarter we concentrated our effort on the development of the three inch diameter flat cylindrical cell for the GLLD Laser Designator Battery. We initiated procurement of parts during the first quarter. The detailed design of the flat cell and its parts, as well as the design and fabrication of tooling needed to make the parts and cell was mostly completed during the third quarter. We have developed two types of flat cell, one is 0.45 inch thick while the other is 0.90 inch thick. The packaging efficiency of the battery with 0.90 inch cells is substantially higher than with 0.45 inch cells. Construction and performance characteristics of both types of flat cells were described in the report for the third quarter.

During the first two quarters we also examined the cell reaction mechanism using cyclic voltammetry. The information gained from this study indicated several approaches for improving both performance and safety of $Li/SOCl_2$ cells. We evaluated the efficacy of these approaches during the third quarter and found that both performance and abuse resistance of the cells could be significantly improved by the use of additives. We evaluated some of the promising additives in the three inch diameter flat cell as well. During the fourth quarter we made additional engineering improvements to the 0.9 inch thick flat cell to enhance its performance. We found that the cell capacity and the abuse resistance of the D cell on the GLLD test were increased by the use of cathode additives. We also investigated the use of very long and thin electrodes to increase capacity on the GLLD test, with encouraging results.

During the fifth quarter we developed the D cell further with the aim of creating a cell design combining high capacity on the BA5590 test with the high rate performance necessary for GLLD test. This was done by increasing cathode capacity while maintaining a large electrode area. We also further defined the high rate performance of 0.9 inch flat cylindrical cell with impressive results.

In the sixth quarter we assembled and filled one hundred cells of the D cell design selected for production during the fifth quarter. Storage life of the D cell was demonstrated by abusive storage at 72°C followed by GLLD and BA5590 test. We further defined performance retention of the flat cell after storage during the sixth quarter and further demonstrated the safety of the flat cell package during voltage reversal at 3.2A and 20A.

II. Laser Designator Battery/BA5590 Battery

A. The specifications of the GLLD Laser Designator Battery are as follows:

Dimensions	2.82" x 3.75" x 9.30"	
Voltage 24V nominal		
	Maximum (OCV)	32V
	Average	24V
	End	20V

We considered the following types of individual cells for the above battery:

A. 16 spirally wound D cells; 8 in series, with the two series stacks in parallel.

B. 16 flat cells (3 inch O.D., 0.45 inch thick); 8 in series with the two series stacks in parallel.

C. 8 flat cells (3 inch O.D., 0.90 inch thick) in series.

D. 8 cylindrical 1.8" diameter spirally wound cells in series.

The development of the D cells and the two types of flat cell were described in the four preceding reports (8-11). The original GLLD duty cycle was: 17.5A for 0.0355 sec followed by 1.8A for 0.0145 sec; this cycle continues for 3 minutes. This constitutes one burst. This three minute cycle occurs every thirty minutes. This duty cycle has been changed by the sponsor. The new duty cycle is: 20A for 0.029 sec followed by 3.2A for 0.021 sec; this cycle continues for 20 seconds every three minutes. These duty cycles are shown schematically in Fig. 1. Cell capacities on the new and old GLLD regimes are very similar, while the shorter duration of the burst gives less cell heating with the new regime.

B. The specifications of the BA5590 Manpack Radio Battery are as follows:

Dimensions:	4.4" x 2.45" x 5.00"
Voltage:	Nominal 12 or 24V
	Maximum (OCV) 15 or 30V
	Average 12.5 or 25V

End: 10 or 20V

Capacity at 70°F 10 A.hr (30 hr. rate)

Max. Rate: 2 hr rate

Duty for 30V operation: 8 Ω load for 0.100 sec followed by 39 Ω load for 1 min followed by 560 Ω load for 9 min.
The above is repeated.

The presently used batteries contain 10 Li/SO_2 D cells in series and parallel to meet the 15 and 30V requirements. In view of the higher OCV of the $Li/SOCl_2$ D cells (3.6V) only eight D cells are needed for the required voltage. This in turn requires a cutoff voltage of 2.5V/cell compared to 2.0 for the Li/SO_2 D cell.

III. Spirally Wound D Cell

Introduction

The use of spirally wound D cells is attractive for the GLLD Laser Designator Battery because the technology is well developed. The cell incorporates proven packaging with a hermetic glass-to-metal seal and a low pressure vent which is hermetic until opening on short circuiting or other abusive use. The spirally wound cell is also easy to construct and is thus a convenient vehicle to study the effect of cell construction variables on performance. Finally, the spirally wound $Li/SOCl_2$ D cell can be manufactured at our lithium battery manufacturing facility with a minimum of alterations and new tooling.

We developed the $Li/SOCl_2$ D cell for the BA5590 test during the first two quarters. Cells with improved current collection gave over 10 A.hr on test on the BA5590 test cycle. A test battery of 8 D cells was prepared which ran for over 100 hours on the BA5590 duty cycle.

We have developed the spirally wound D cell for the GLLD application by examining a number of different techniques for cathode current collection and adopting the most satisfactory ones. This gave a D cell which, tested in pairs, gave 5.9A.hr/cell on the GLLD test cycle. We examined a number of cathode additives in the spirally wound D cell which increased cell capacity to 7.3 A.hr with improved abuse resistance during voltage reversal. We then explored the limits of high rate performance for conventional $Li/SOCl_2$ D cells by use of cathode pretreatment and extremely long electrodes to give a D cell providing 8.05-8.4 A.hr on the GLLD test. During the fifth quarter we returned to the BA5590 test and developed the spirally wound D cell for satisfactory performance on both BA5590 and GLLD applications.

We assembled and filled one hundred (100) D cells of the design selected as the optimum during the fifth quarter. These cells were delivered to the sponsor. We continued to evaluate this D cell design to demonstrate performance on the GLLD and BA5590 tests after abusive storage at 72°C.

Experimental

The D cells were of the now familiar spirally wound construction which is hermetically sealed and incorporates a glass-to-metal seal for electrical isolation of the electrodes and a second glass to metal seal serving as a low pressure vent to prevent explosions on shorting.

We tested the D cells on the BA5590 duty cycle using a relay and mechanical timer and on the GLLD test cycle using a micro-processor controlled pulse discharger we built for this purpose.

Cells were stored at 72°C in a Blue-M oven and tested at -30°C in a Blue-M Versa-Range Test Chamber. Data were recorded on Gould high speed recorders.

Results and Discussion

The cell design selected for the production order combines good performance on the BA5590 and GLLD test with ease of assembly. The final cell design incorporates a 26" cathode with optimized current collection for high rate performance with an anode/electrolyte excess design which we demonstrated earlier (7) to provide improved abuse resistance during overdischarge.

We earlier demonstrated a fresh cell capacity of over 7 A.hr on the GLLD test and 12 A.hr on the BA5590 duty cycle. We stored a D cell at 72°C for two weeks, allowed the cell to stand for a week, then tested it on the BA5590 duty cycle as shown in Fig. 2. The cell delivered 110 hours of service to a 2.5V cutoff, a capacity of over 12 A.hr. The well known voltage delay phenomenon is shown only on the 1Ω load, and even at 1Ω, load voltage is over 3V after $\sim$ 2 hours. The load voltage is always over 2.5V and thus there should be a little or no start-up problem. This test shows very good capacity retention

for the cell on the BA5590 loads after high temperature storage. A second D cell was stored at 72° C for two weeks and discharged on the BA5590 load test at -30° C after 6 weeks at room temperature, as shown in Fig. 3. This cell delivered 8.8 A.hr to 2.0V, or over 70% of the fresh cell capacity on the same test at room temperature, once more demonstrating the good capacity retention of this design.

We stored a pair of D cells at 72° C for two weeks and then tested the cells on the GLLD duty cycle at room temperature as shown in Fig. 4. The capacity realized on this high rate test was 6.8 A.Hr/cell to a 2.5V cutoff, over 90% of the fresh cell capacity. Some voltage delay was observed early in the test, but a load voltage of 2.0V at 20A was reached in 12 minutes and 2.5V in 2-1/2 hours. The capacity at 20A above 2.0V was higher, 8.6 A.hr/cell, which is very comparable to capacities above 2.0V at 20A for unstored cells, showing once more the very good capacity retention of the high rate D cell on abusive storage.

We stored a further pair of D cells at 72° C for two weeks, followed by six weeks at room temperature. These cells were then equilibrated at -30° C and discharged on the GLLD duty cycle at -30° C as shown in Fig. 5. The cell capacity on the GLLD test was very low, with the 20A load voltage never reaching 2.5V and the capacity above 2.0V only 1.8 A.hr. At lower currents and voltages the cells showed higher capacity. There was also some delay in the cells reaching their running voltage at 20A, although there was much less delay at 3.2A.

Conclusion

During the sixth quarter we fabricated and delivered one hundred (100) D cells of best design, as called for by the sponsor. We also demonstrated the good capacity retention of these cells after abusive storage at 72° C on both the BA5590 and GLLD simulated loads.

IV. The Flat Cylindrical Cell

Introduction

We have developed the flat cylindrical cell, 3 inch in diameter and 0.9 inch thick, for the GLLD Laser Designator application. The details of the construction of the cell are described in the previous reports (9-11). The cell weighs approximately 225 gm. We optimized the internal electrode structures of this cell in order to obtain the best performance on GLLD load regime. The internal impedance of the cell was extremely low thus leading to a very low cell polarization and minimum cell heating on the GLLD load. The performance of the cell, as reported in the fourth quarterly report (11) was found to be outstanding. The cell delivered 300 pulses corresponding to a capacity of 21 A.hr at room temperature.

During the fifth quarter, we evaluated the performance characteristics of the above flat cell at low temperatures, voltage reversal, short circuit, and high current discharge. During the sixth quarter we evaluated the capacity retention of the flat cell at various temperatures after room temperature storage and capacity retention at room temperature after abusive storage at 72°C. We also investigated high temperature (50°C) discharge of a flat cell on the GLLD duty cycle and safety of the flat cell during voltage reversal on the GLLD test.

Experimental

The flat cylindrical cells were fabricated and assembled as described in earlier reports. These cells are of welded hermetic construction and incorporate a glass-to-metal seal feedthrough which serves as a vent and provides for electrical isolation of the anode and cathode. Discharge tests were performed as described for the high rate D cells.

Results and Discussion

The voltage-time behavior of two typical flat cylindrical cells on the GLLD test are shown in Figures 6 and 7. These cells were both discharged shortly

afrer filling with 1.8M $LiAlCl_4$ in $SOCl_2$. The cell capacities of 18.0 and 19.0 A.hr are typical of test results for flat cylindrical cells although some cells have given as much as 21.3 A.hr on this test. Both cells show the very flat voltages at high currents typical of the very high rate flat cell design. A flat cell was discharged on the GLLD test at room temperature after three days of room temperature storage as shown in Fig. 8. This cell delivered 16 A.hr to a 2.5V cutoff and 19.8 A.hr to 2V. There is also an apparent plateau near the end of the cells' discharge. Another flat cell was tested on the GLLD duty cycle after one week of storage at room temperature as shown in Fig. 9. This cell gave 14.2 A.hr to 2.5V and 16.1 A.hr to 2.0V with the apparent plateau in cell voltage at 20A occurring somewhat earlier. The second flat cell was stored for one week after filling and then discharged on the GLLD rate at room temperature as shown in Fig. 10. This cell delivered 20.8 A.hr to a 2.5V cutoff and showed no evidence of any voltage plateau at 20A. This cell was then driven into voltage reversal at the conclusion of the GLLD test. After 4 hours in reversal the cell vented. We continued storage of flat cells at room temperature and found that the behavior of this cell was exceptional. Cells were stored at room temperature for 2, 3 and 6 weeks, then discharged on the GLLD test as shown in Figures 11, 12 and 13 respectively. In each case a decreased cell capacity was observed with the cells giving 11.4, 14.2 and 16.3 A.hr to 2.5V, respectively. The capacity decline is clearly not a simple function of storage time as shown in Fig. 13. Capacities to a 2.0 cutoff were much more reproducible at 16.8, 17.5 and 17.5 A.hr, indicating the storage phenomenon is more of a decline in rate performance of the cell than a loss in coulombic capacity per se. The cell stored six weeks in Fig. 13 was tested on a slightly different discharge regime with the same loads, but 2 pulses every 3 minutes.

We have further explored the performance of these cells on storage by discharging on GLLD test at 0°C a cell which had been stored at room temperature for three weeks. This cell delivered 7.8 A.hr to 2.5V and 12.8 A.hr to 2.0V as shown in Fig. 15, with the lower voltage plateau at 20A being quite marked. We stored another flat cell for two days at 50°C and two days at 72°C to simulate abusive storage, then discharged the cell on the GLLD test regime at room temperature. During storage there was no can bulging, while pressure inside

the cell never exceeded 50 psi. The cell capacity, as shown in Fig. 16, was 16.8 A.hr to 2.5V and 18.5 A.hr to 2.0V, shown no greater deterioration in performance on high temperature storage. The cell required less than 15 minutes to reach load voltage of 2.5 at 20A. The cell internal pressure and the wall temperature were monitored during the discharge. Note, that the cell internal pressure rose very rapidly towards the end of the discharge, remaining below 100 psi up to the 2.0 volt cutoff point.

We stored a flat cell with cathode additive 1 for two days at 72°C and 3-1/2 days at room temperature. This cell gave a capacity of 10.5% A.hr to 2.5V on the GLLD test and 14.7 A.hr to 2.0V as shown in Fig. 17. While the use of cathode additives gave improved performance in the D cell on the GLLD test, the flat cell is not cathode limited in the sense of the D cell design, and no performance improvement was expected. The lower voltage plateaus were quite apparent in this cell.

We constructed a flat cell in which the cathodes were scrupulously dried in a vacuum oven. This cell was stored for 1 day at 72°C and 3-1/2 days at ambient before being discharged on the GLLD test. This cell delivered 14.4 A.hr to 2.5V and 17.8 A.hr to 2.0V as shown in Fig. 18. The loss of rate performance vis-a-vis a fresh cell shows that excess water contamination is not the source for flat cell rate deterioration on storage.

We stored a flat cell for three weeks at room temperature and then discharged the cell at an elevated temperature of 48°C as shown in Fig. 19. This cell demonstrated quite good performance, delivering 19.9 A.hr to 2.5V and over 21 A.hr to 2.0V on the GLLD test. The cell temperature rose to 55°C during the course of the test, while capacity was equal to that of a fresh cell.

Several cells were prepared using 1<u>M</u> $LiAlCl_4$ in $SOCl_2$ as the electrolyte solution. The discharge performance of a fresh cell and one stored for two weeks at room temperature are compared in Figures 20 and 21. The cell capacities were limited due to the lower electrolyte conductivity, but there was no discernible drop in capacity or rate on storage. At this point it is clear that there exists a problem with the 3 inch diameter flat cylindrical

cell in that the rate performance of the cell appears to drop significantly on storage. As seen in Fig. 14, the extent of this decline is not a simple function of temperature, nor is cell performance degraded to the level of the D cell. We have determined that water in the electrolyte or in the porous cathode matrix is not the cause of the problem. We are modifying our method of making internal connections in the cell to get more reliable high rate performance.

We have been particularly concerned with the safety of the flat cell during voltage reversal, especially during overdischarge on the GLLD test. We used a 12V automobile battery to drive a flat cell into reversal on the GLLD test. A flat cell was discharged and driven into reversal on the modified GLLD test using two bursts every three minutes, delivering 16.3 A.hr to 2.5V. The behavior of the cell on voltage reversal is shown in Fig. 22. As shown in Fig. 22 the voltage at 3.2A stays near 0V while the 20A voltage becomes successively more negative before the cell vented at -3.25V after 1.4 hours in reversal. The cell temperature peaked at ~ 75°C during the first hour of reversal and had declined to ~ 60°C when venting occurred. This venting occurred through a hole in the can which developed opposite the G/M seal and centerpost. This particular cell had an anode capacity of some 27 A.hr, which apparently was not an adequate lithium excess to prevent venting. The vented cell is shown in Fig. 23, in comparison with a fresh cell.

Two further flat cells were also driven into reversal at the GLLD rate, as shown in Figures 24 and 25. Both of these cells passed through a temperature maximum about 1 hour into reversal with a pressure maximum near 215 psi. In both of these cells the voltages in reversal stabilized near -0.2V at 20A and 0.0V at 3.2 A. The cells continued in reversal with no evidence of venting for 16 and 40 hours respectively before the tests were terminated. The cells appear to form an internal short circuit by electrodeposited Li in the cathode. This process results in the cell showing an OCV of 0.0 and a very low resistance. With the voltage thus clamped and internal heating negated the cell can run in reversal for an indefinite period of time. Both of these cells contained some 45 A.hr of lithium, a substantial amount in excess of the cell capacity for $SOCl_2$.

We also drove a flat cell into reversal at a steady current of 20 A, after it was discharged on the GLLD test, as shown in Fig. 26. During the reversal voltage clamped near -0.3V as temperature rose to 68°C in the course of the 35 minute cell reversal at 20 A. Once more the lithium excess design (32 A.hr) prevented cell venting or explosion during the voltage reversal.

Conclusion

During the sixth quarter of the contract we investigated the storage and safety characteristics of the three inch flat cylindrical cell. We found that the cells' high rate capacity declines somewhat on storage, even at room temperature although the coulombic capacity of the cell remains undiminished. This effect shows up only on the 20 A load and manifests itself as an increased capacity between 2.5 and 2.0V on the GLLD test at 20 A. The loss in rate performance is not very reproducible. We are modifying our internal cell design to minimize the loss of high rate performance.

We also investigated the safety of the flat cell during voltage reversal at the GLLD currents of 3.2 A and 20 A. We found the flat cell configuration to be safe against venting or explosion provided proper materials loadings were observed in the cell.

V. Conclusion

During the sixth quarter of this contract we fulfilled production requirements by delivering 100 D cells of best design to the sponsor. We continued to characterize the optimum D cell design, particularly through emphasis on capacity retention after abusive storage at 72°C. The cells demonstrated excellent capacity retention after two weeks at 72°C on room temperature test and somewhat lower capacities at lower test temperatures.

We demonstrated the safety of the flat cylindrical cell during abusive overdischarge at 3.2 and 20 Amps. Cells with proper materials loadings were demonstrated not to vent or explode under reversal at the GLLD rates. We also found that the high rate performance of the flat cell declines on storage in an irregular fashion.

Both the flat cell and D cell have been demonstrated to fulfill the high rate requirements of the BA5590 and GLLD applications. These cells successfully combine high rate performance with safety as shown by behavior during a variety of abusive tests.

VI. References

1. W. K. Behl, J. A. Cristopulos, M. Ramirez and S. Gilman, J. Electrochem. Soc., 120, 1619 (1973).

2. J. J. Auborn, K. W. French, S. I. Lieberman, V. K. Shah and A. Heller, ibid, 120, 1613 (1973).

3. D. L. Maricle et al, U. S. Pat. 3, 567, 515 (1971); G. E. Blomgren and M. L. Kronenberg, German Pat. 2, 262, 256 (1973).

4. A. N. Dey and C. R. Schlaikjer, Proc. 26th Power Sources Symposium, Atlantic City, April 1974.

5. C. R. Schlaikjer, U. S. Pat. 4, 020, 240 (1977), Proc. 28th Power Sources Symposium, Atlantic City, June 1978.

6. J P. Gabano and P. Lenfant, Abstract No. 27, Electrochemical Society Meeting, Pittsburg, PA., Oct. 1978.

7. A. N. Dey, "Sealed Primary Lithium Inorganic Electrolyte Cell" Final Report, DELET-TR-74-0109-F, P. R. Mallory & Co., Inc. July 1978.

8. A. N. Dey, W. Bowden, J. Miller, P. Witalis, "Lithium-Thionyl Chloride Battery", ERADCOM, DELET-TR-78-0563-1, First Quarterly Report, P. R. Mallory & Co. Inc., April, 1979.

9. A. N. Dey, W. Bowden, J. Miller, P. Witalis, "Lithium-Thionyl Chloride Battery", ERADCOM, DELET-TR-78-0563-2, Second Quarterly Report, P. R. Mallory & Co. Inc., July, 1979.

10. A. N. Dey, N. Hamilton, W. Bowden, P. Witalis, "Lithium-Thionyl Chloride Battery", ERADCOM, DELET-TR-78-0563-3, Third Quarterly Report, P. R. Mallory & Co. Inc., July, 1979.

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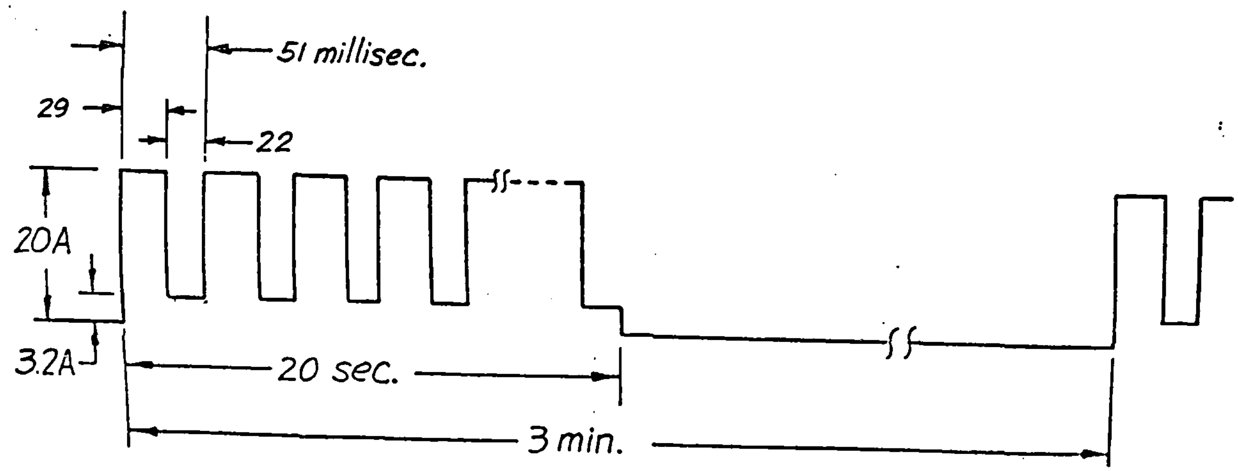

Fig. 1. Schematic diagram for the pulse discharge in the new GLLD duty cycle

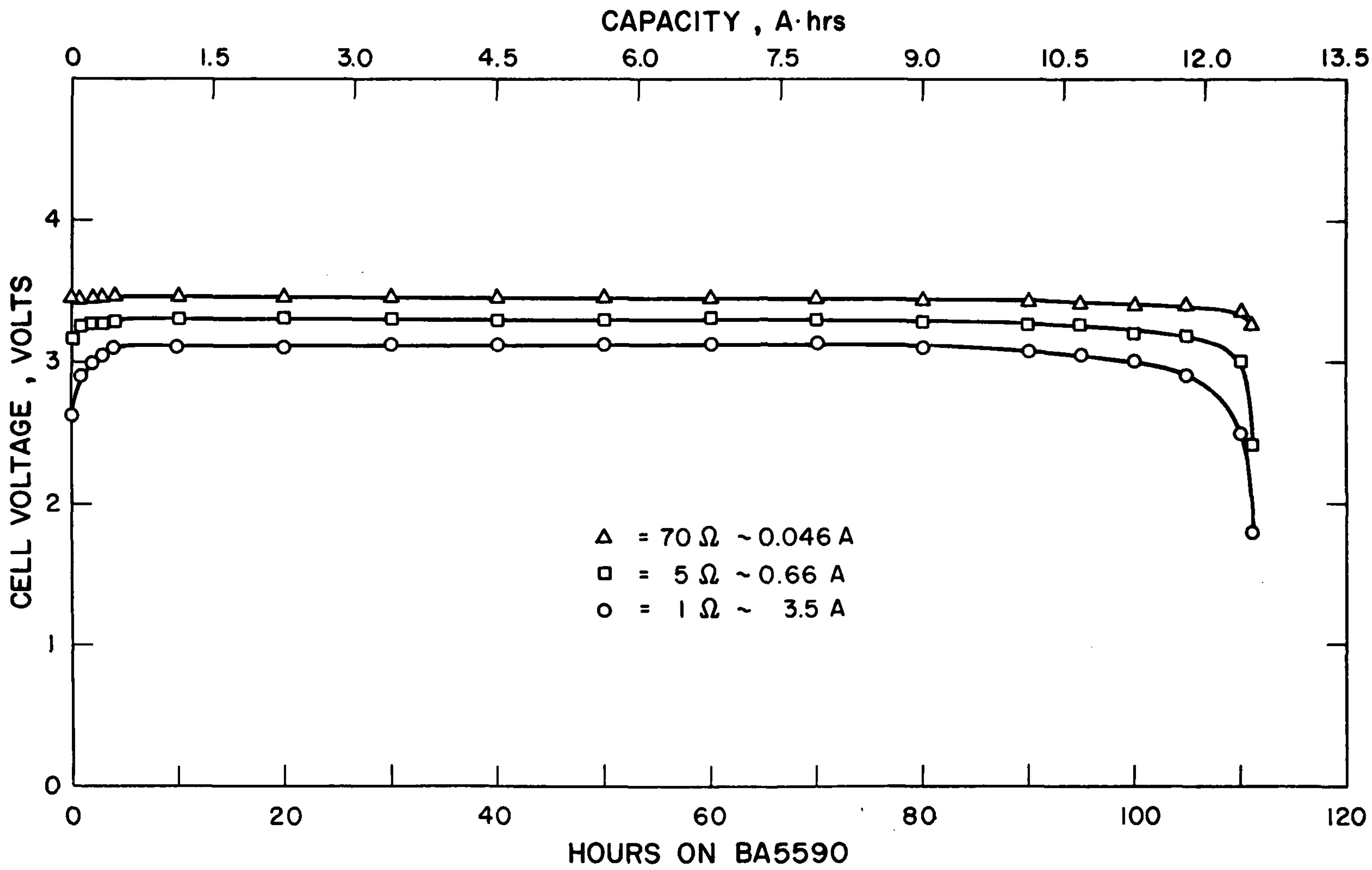

Fig. 2. Performance of a high rate D cell on the BA5590 test after two weeks at 72°C

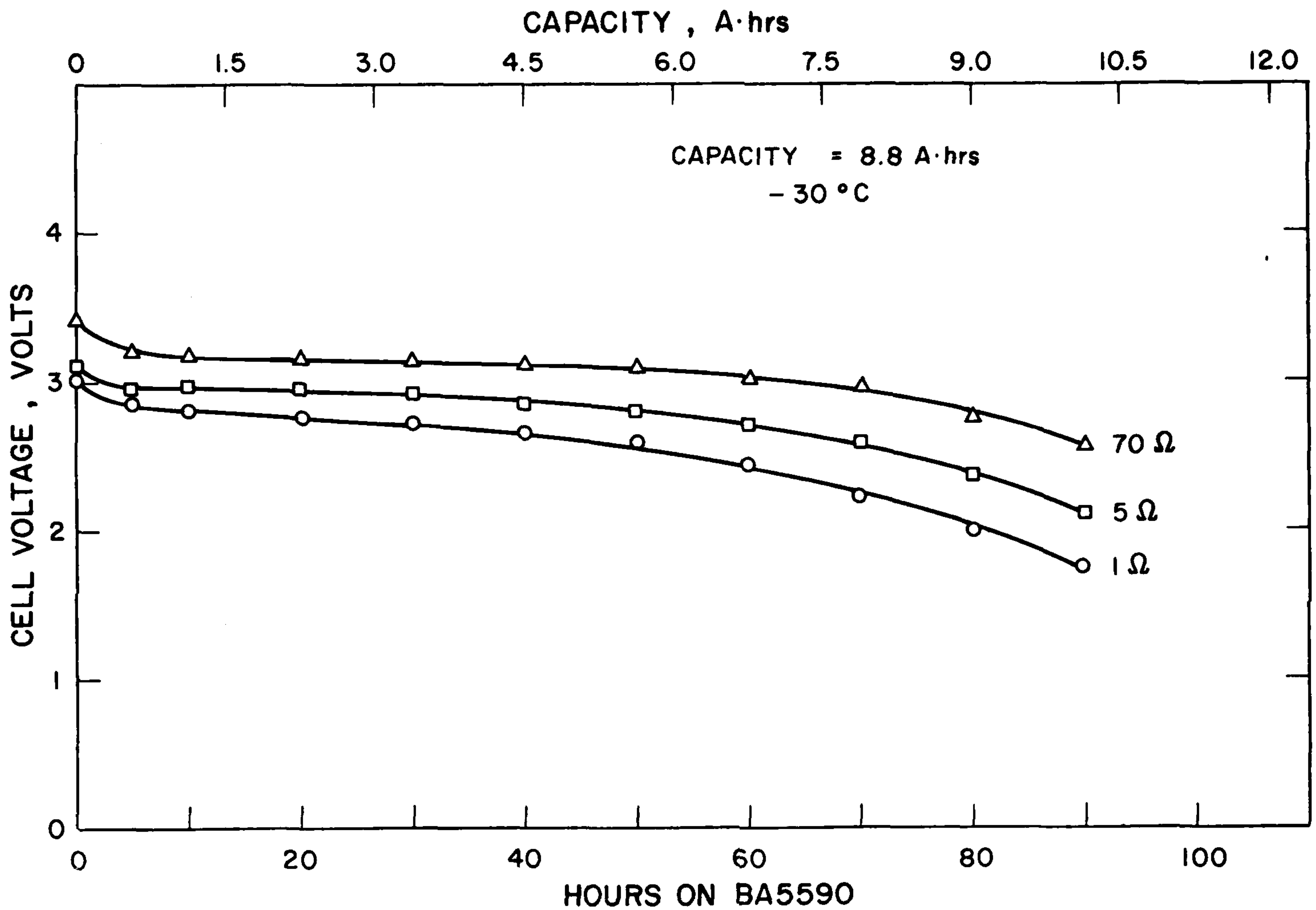

Fig. 3. Performance of a D cell at -30=C on the BA5590 test after two weeks storage at 72°C

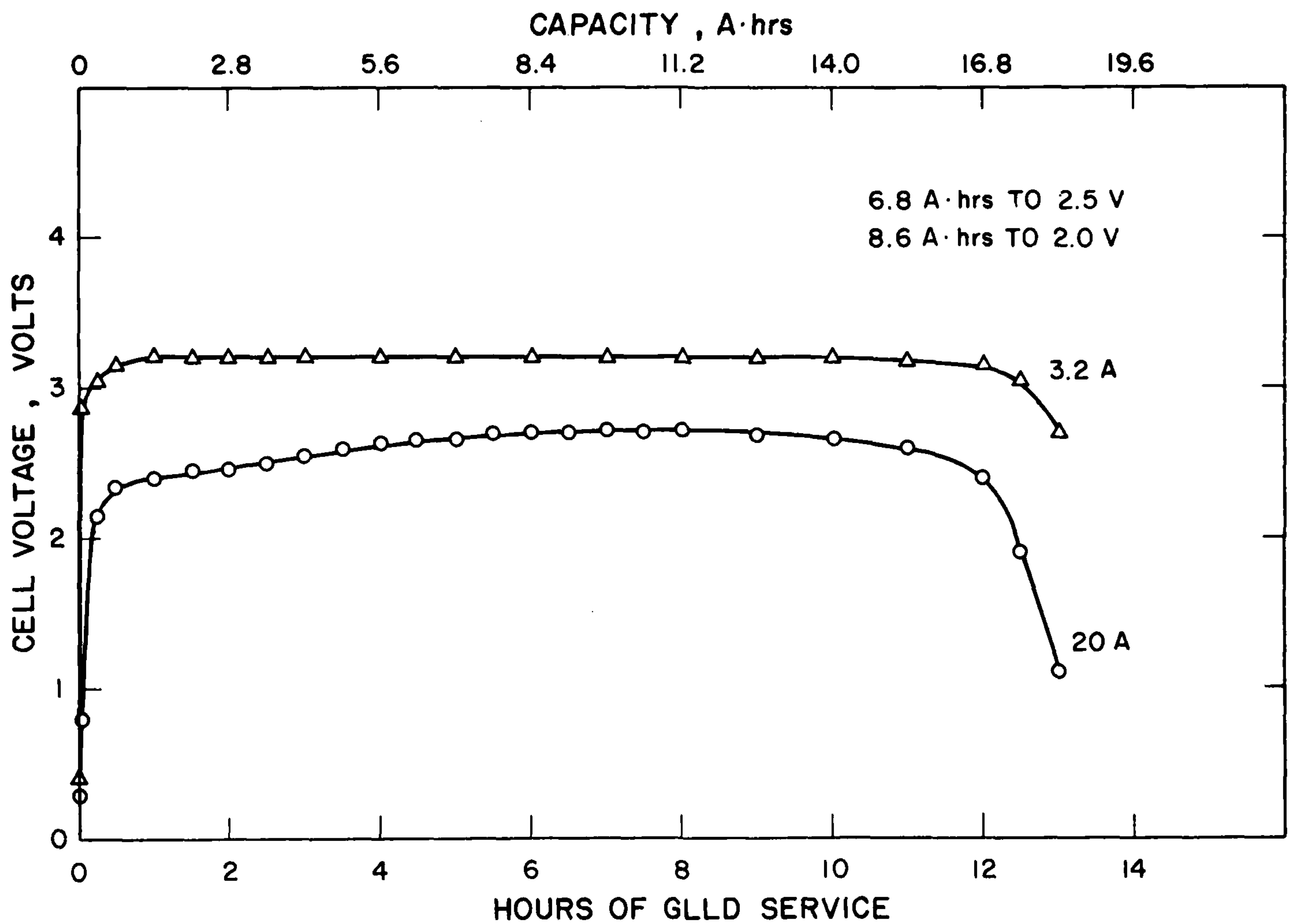

Fig. 4. Performance of a pair of D cells on the GLLD test after two weeks storage at 72°C

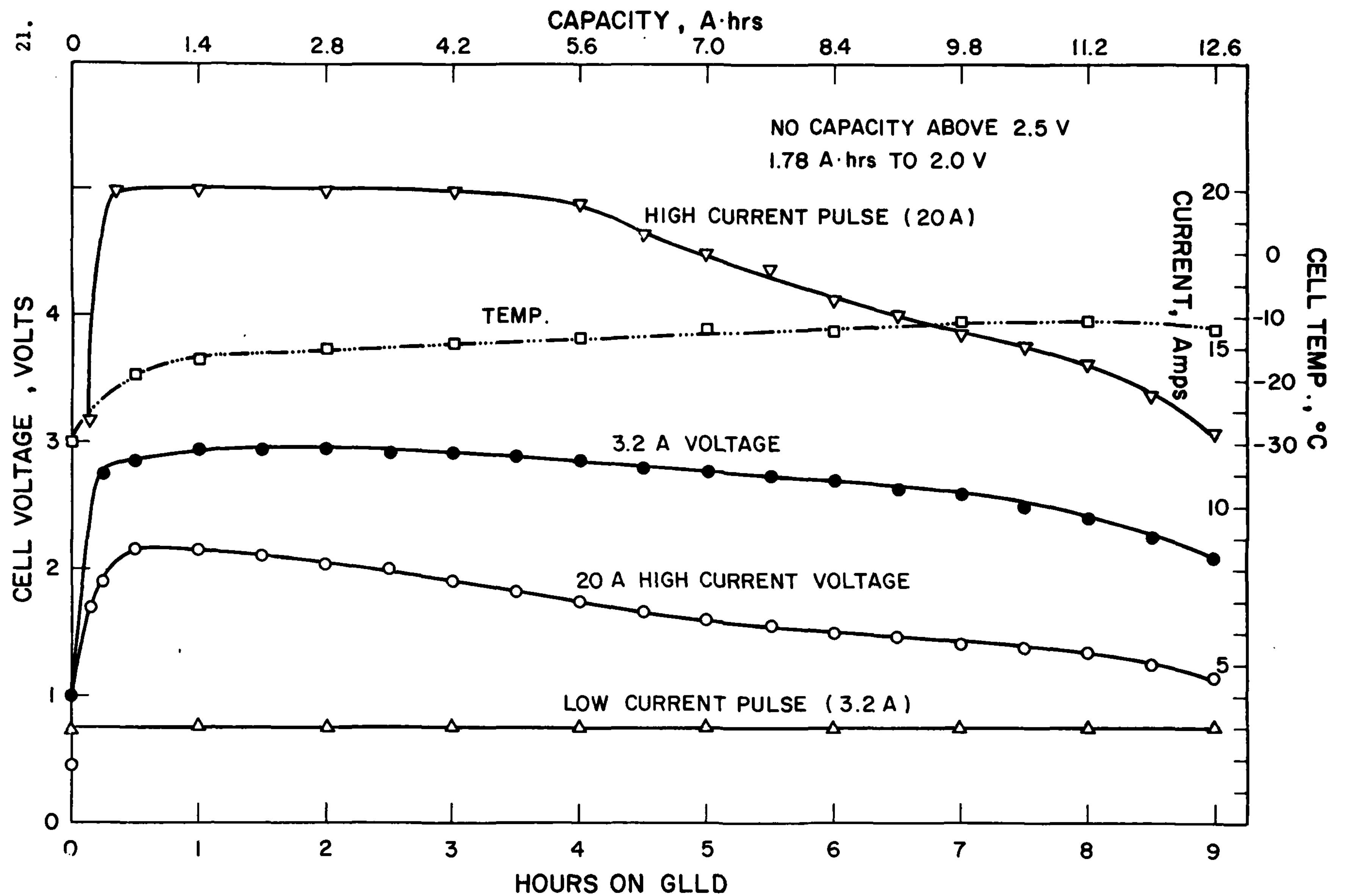

Fig. 5. Performance of a pair of D cells on the GLLD test at -30°C after two weeks of storage at 72°C

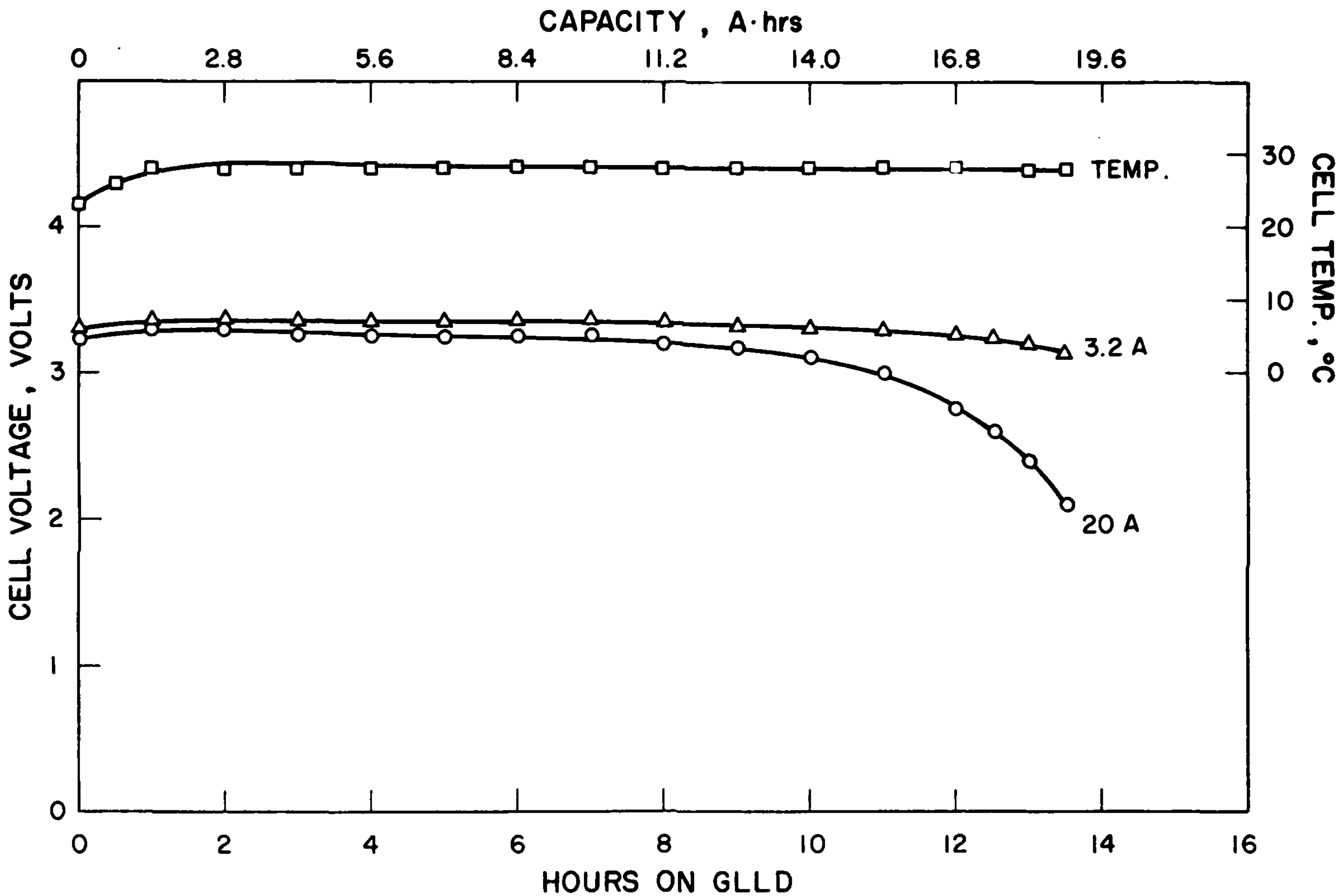

Fig. 6. Performance of fresh flat cell on the GLLD test at room temperature

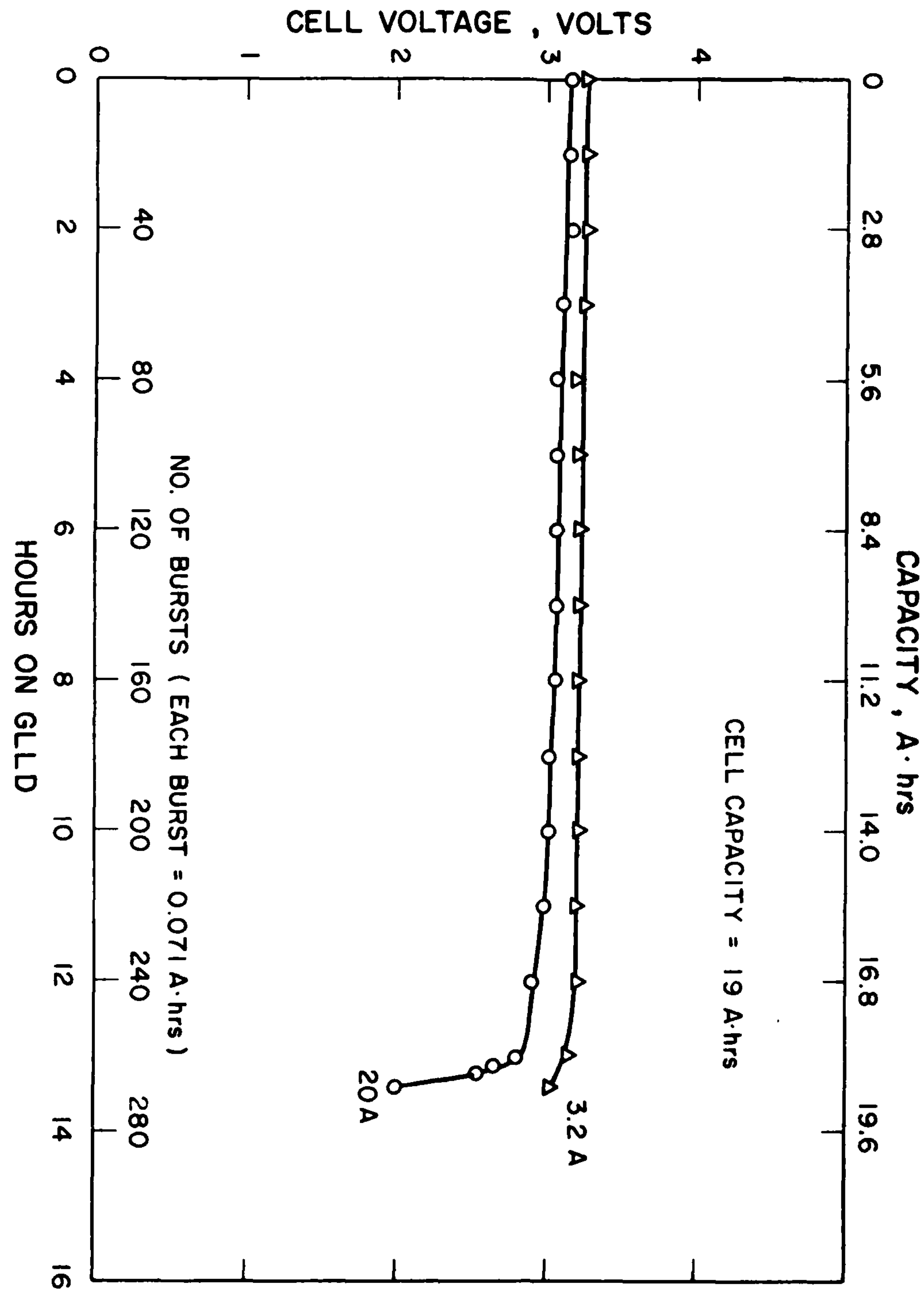

Fig. 7. Performance of a fresh flat cell on the GLLD test at room temperature

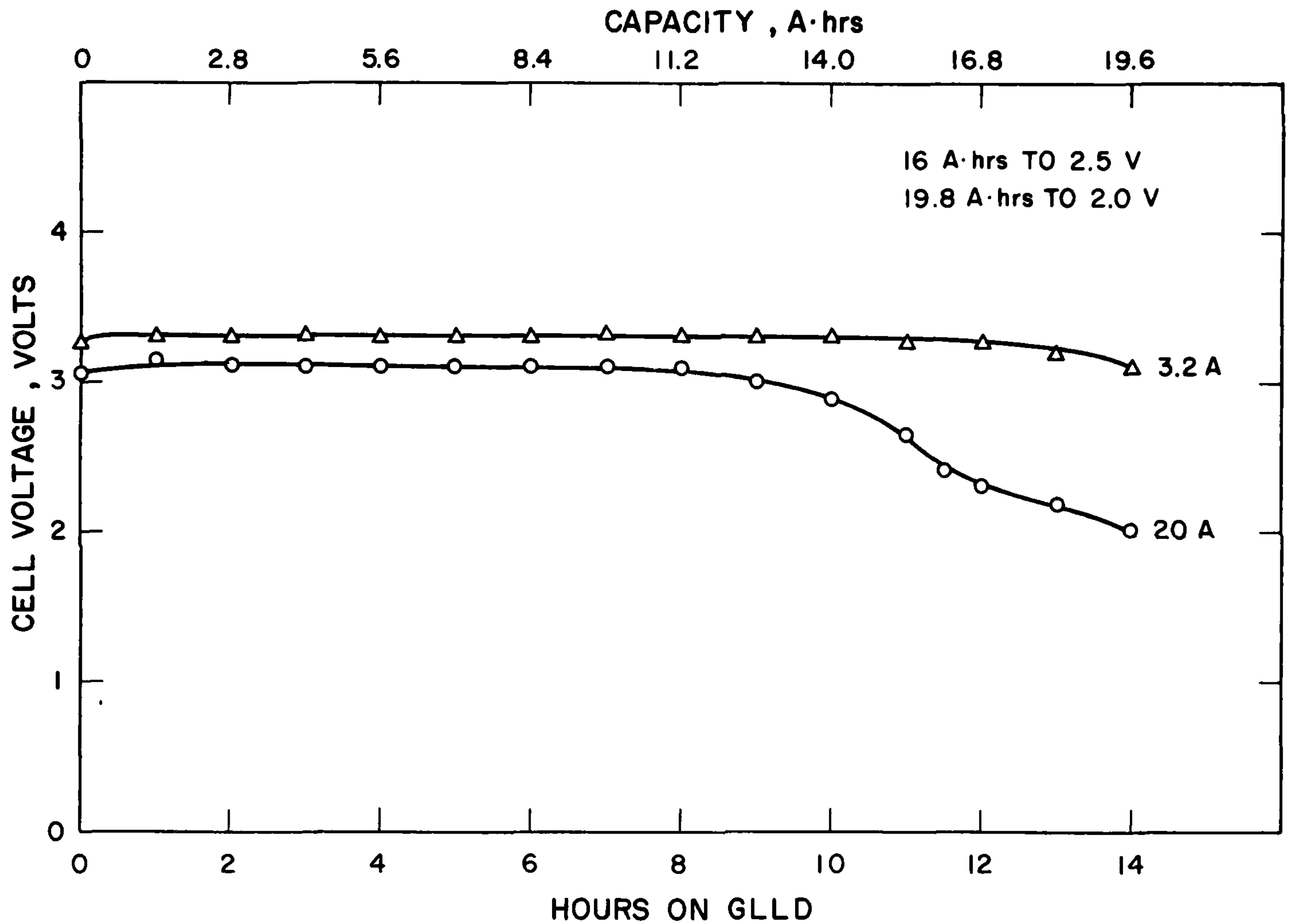

Fig. 8. Performance of a flat cell on the GLLD test at room temperature after three days at room temperature

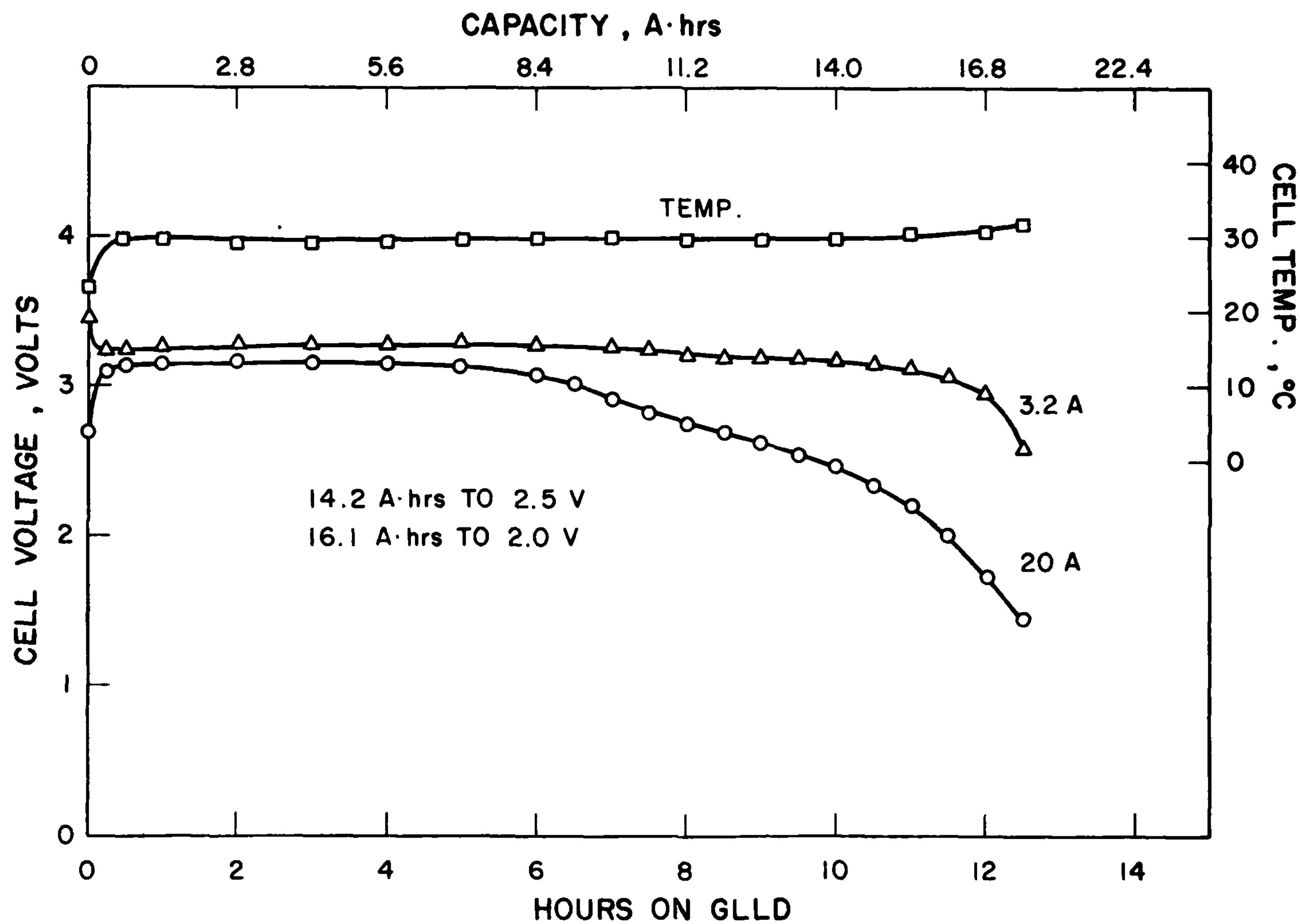

Fig. 9. Performance of a flat cell on the GLLD test at room temperature after one week at room temperature

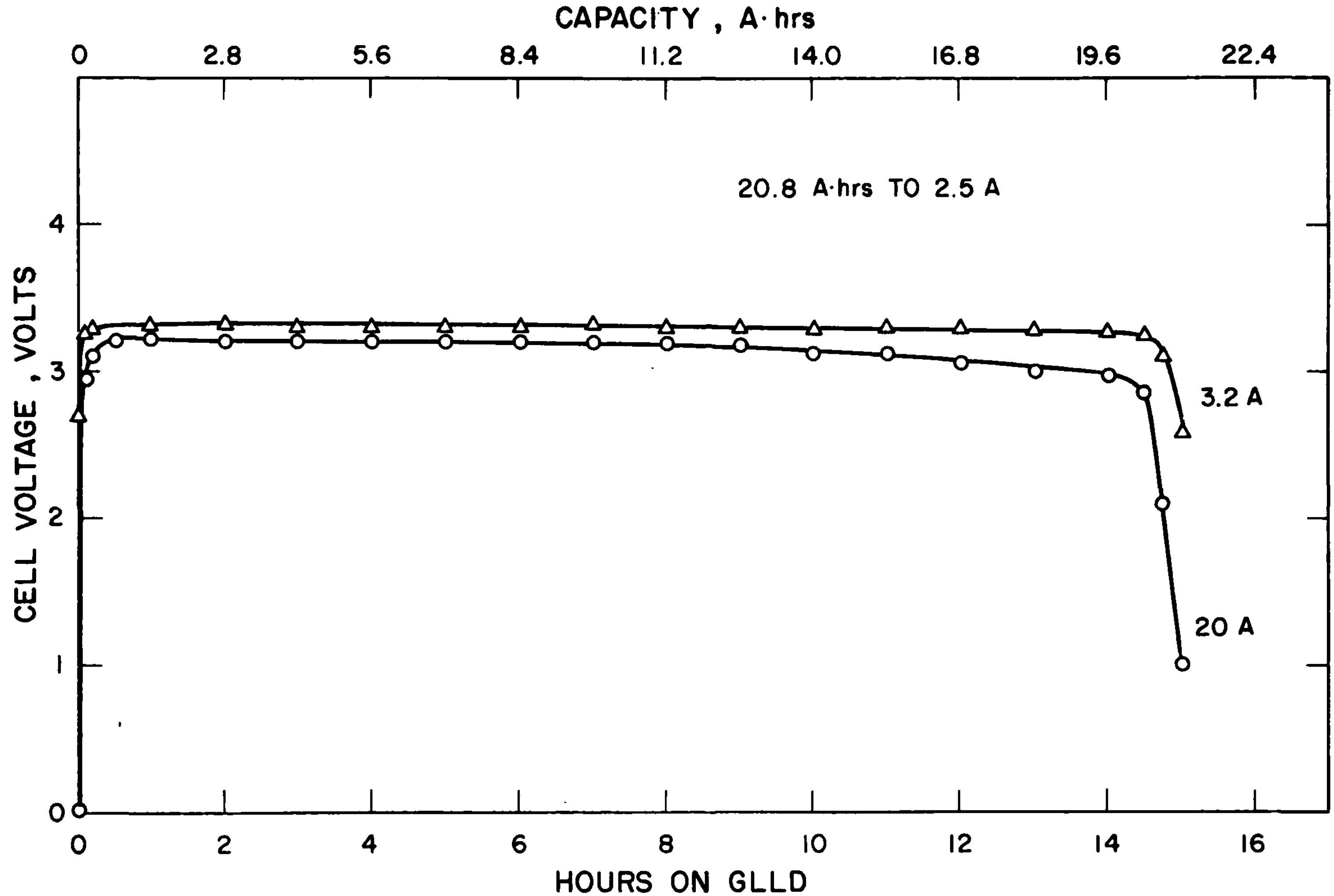

Fig. 10. Performance of a flat cell on the GLLD test at room temperature after one week at room temperature.

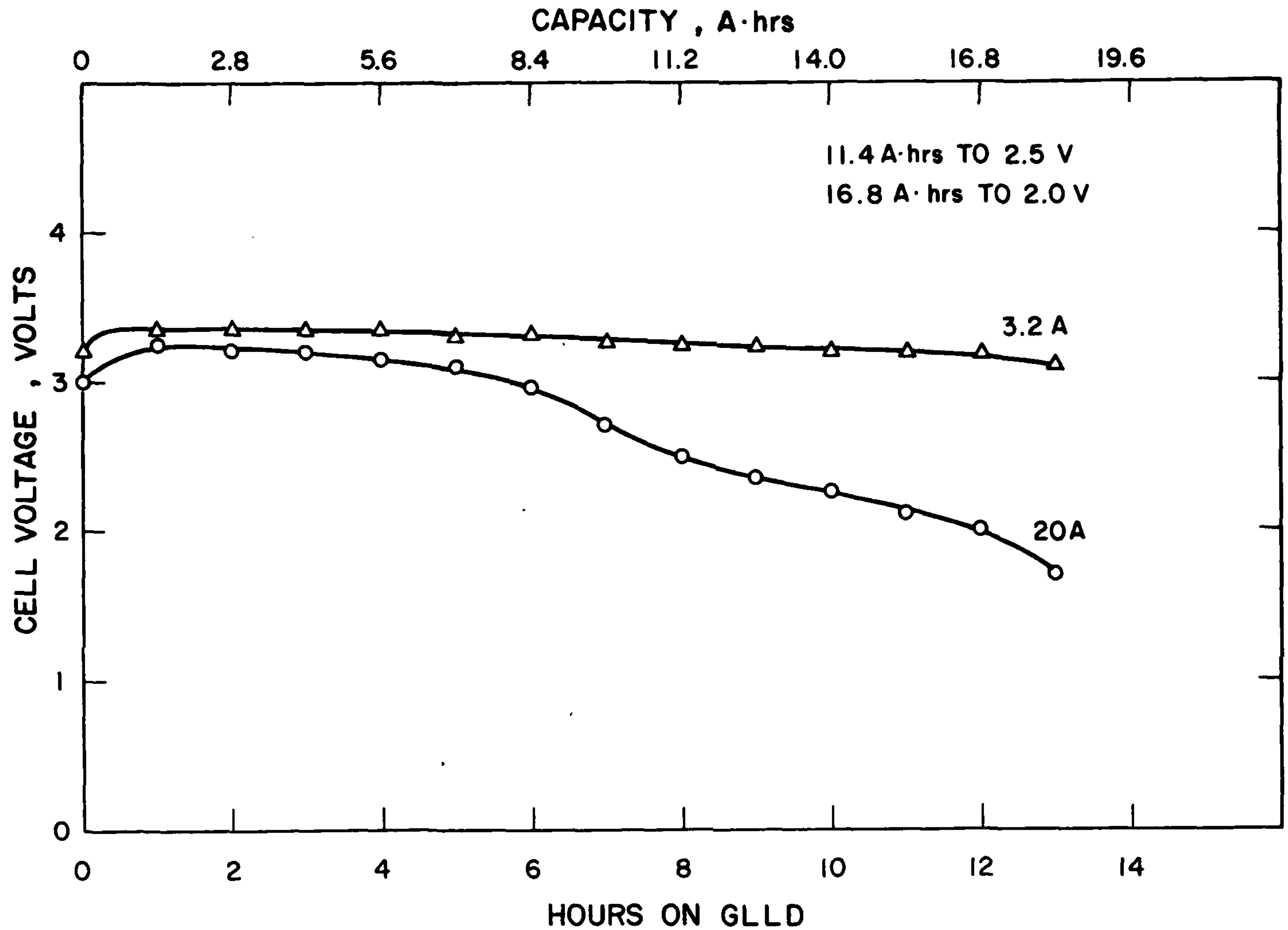

Fig. 11. Performance of a flat cell on the GLLD test at room temperature after two weeks at room temperature

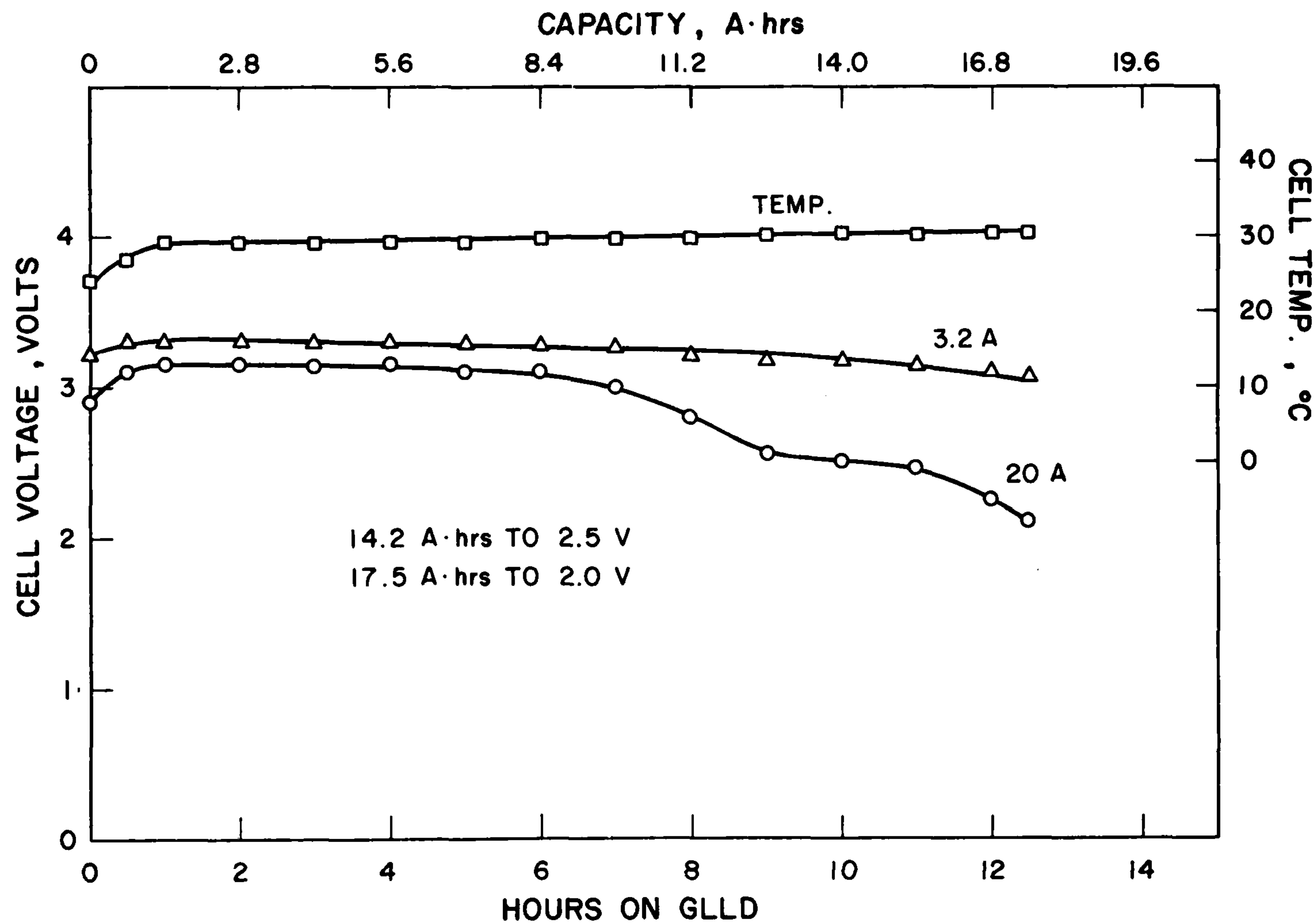

Fig. 12. Performance of a flat cell on the GLLD test at room temperature after three weeks at room temperature

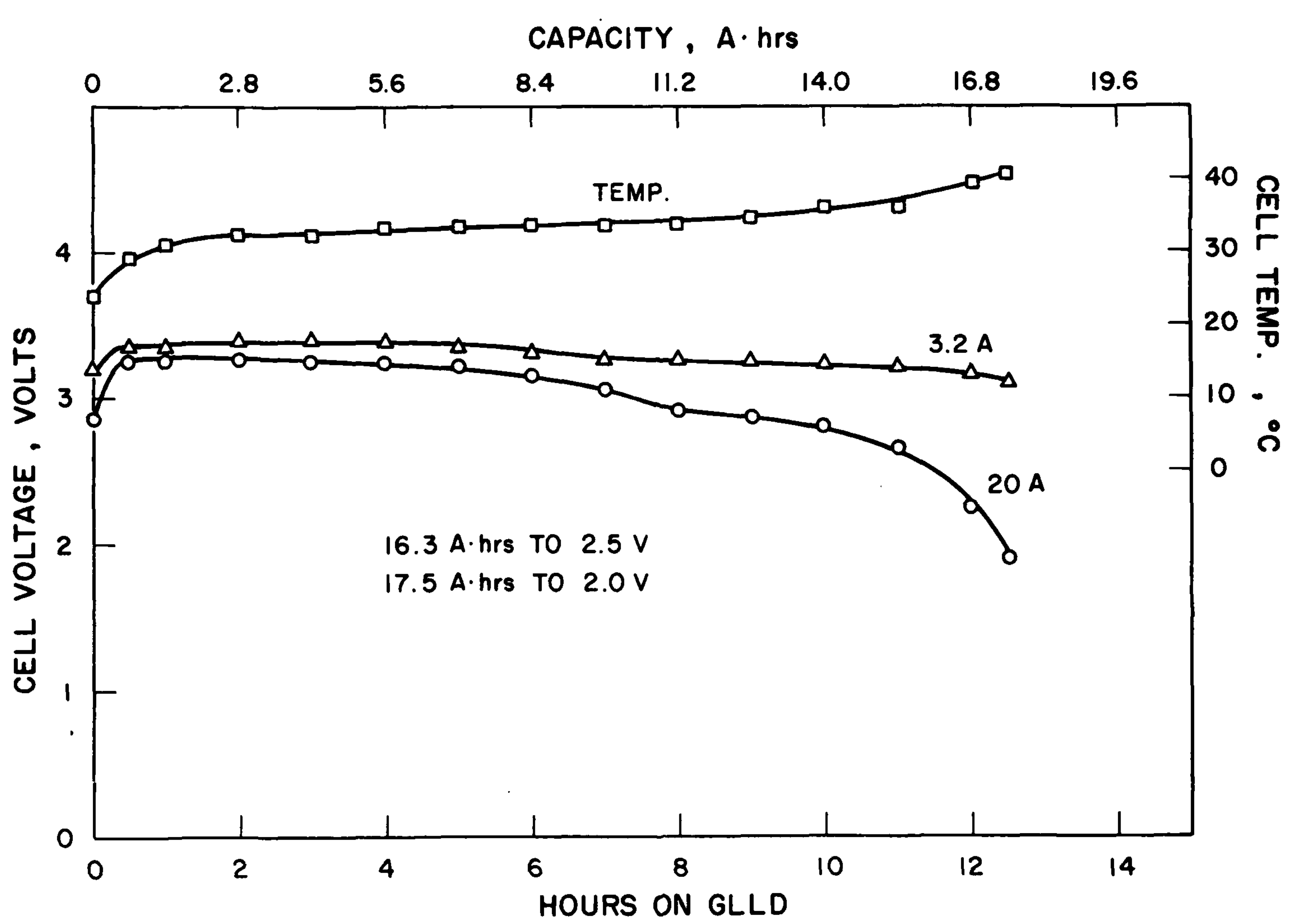

Fig. 13. Performance of a flat cell on the GLLD test at room temperature after six weeks at room temperature

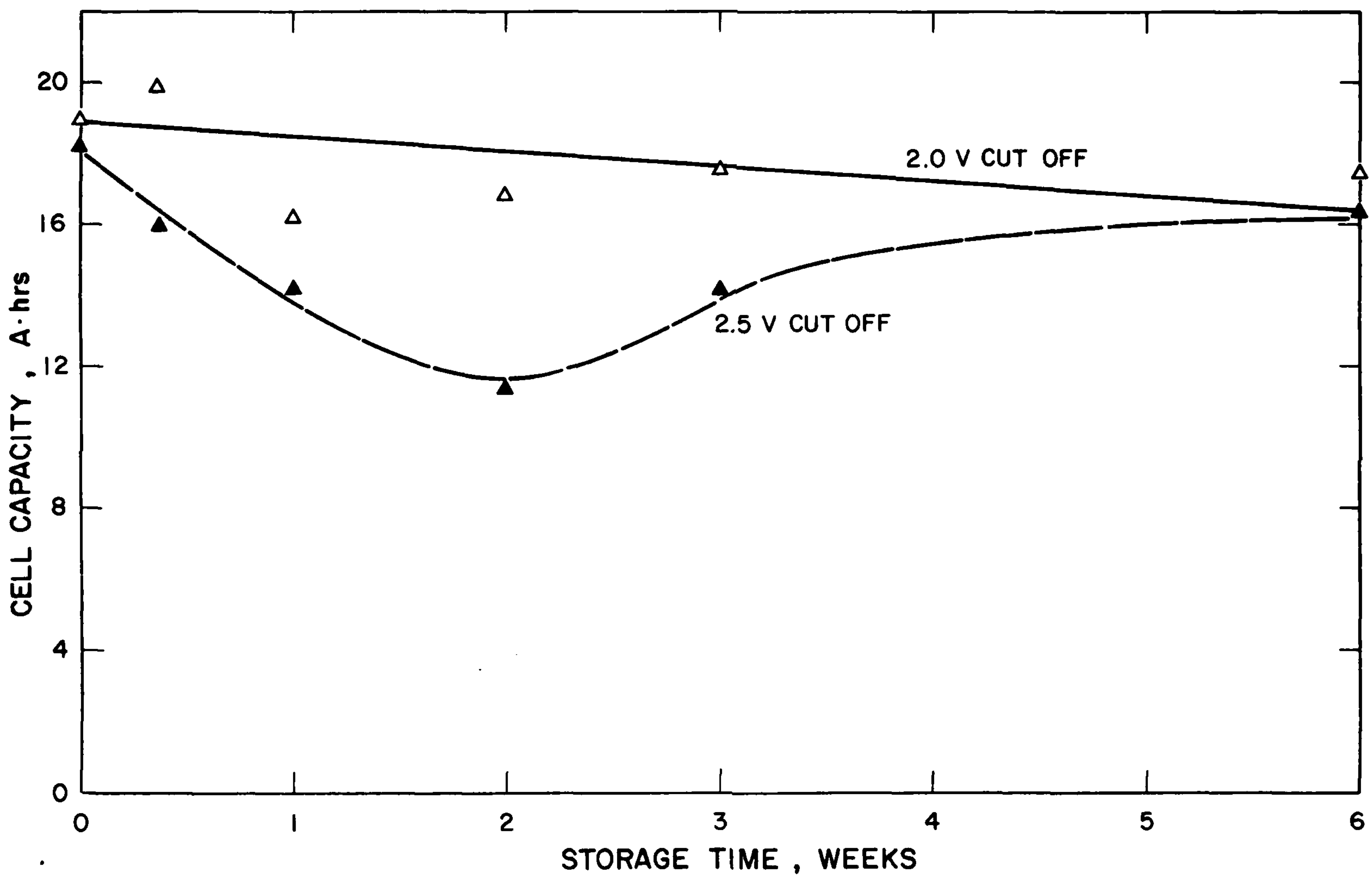

Fig. 14. Plot of capacity on GLLD test vs. storage time for flat cylindrical cells

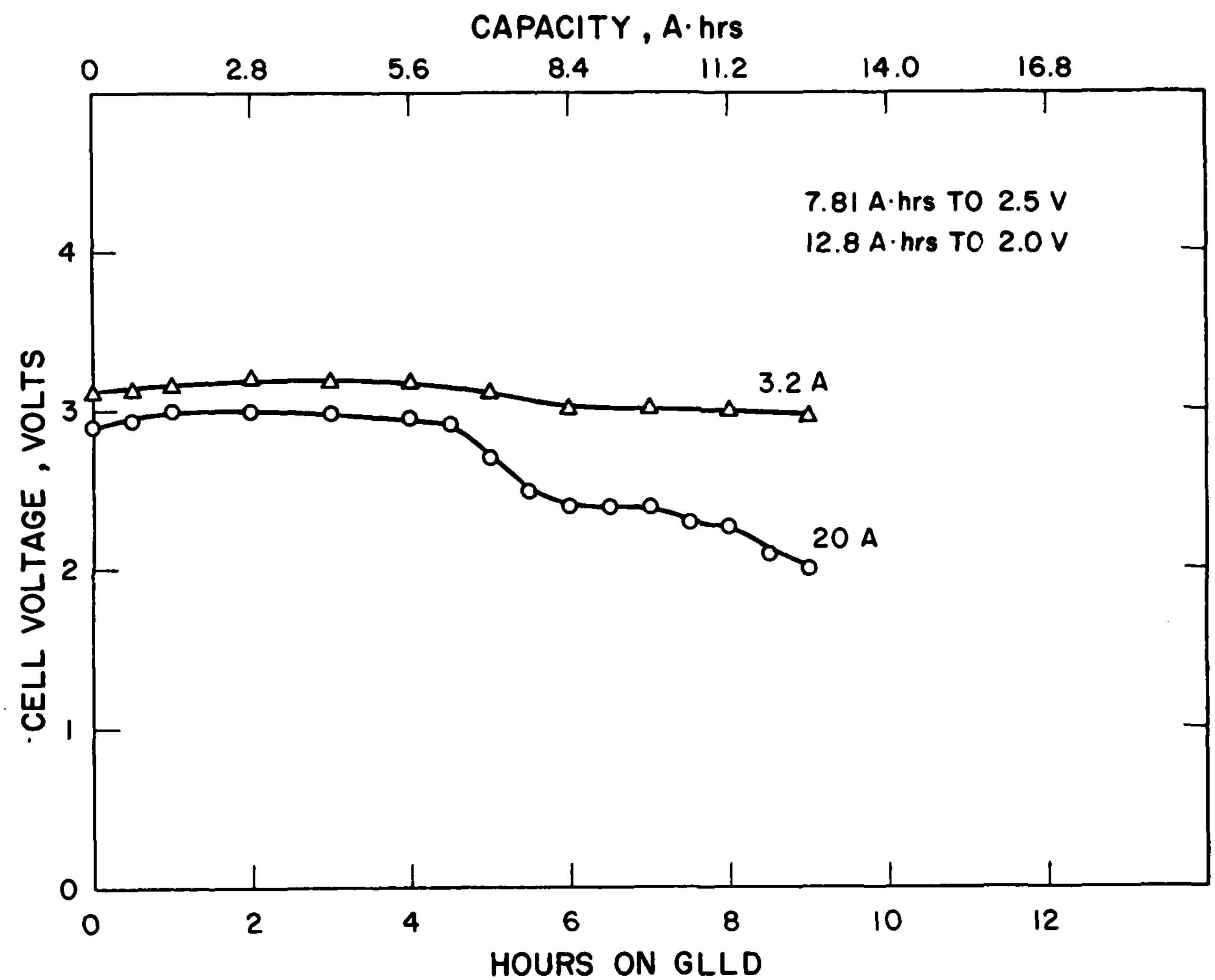

Fig. 15. Performance of a flat cell on GLLD test at 0°C after three weeks at room temperature

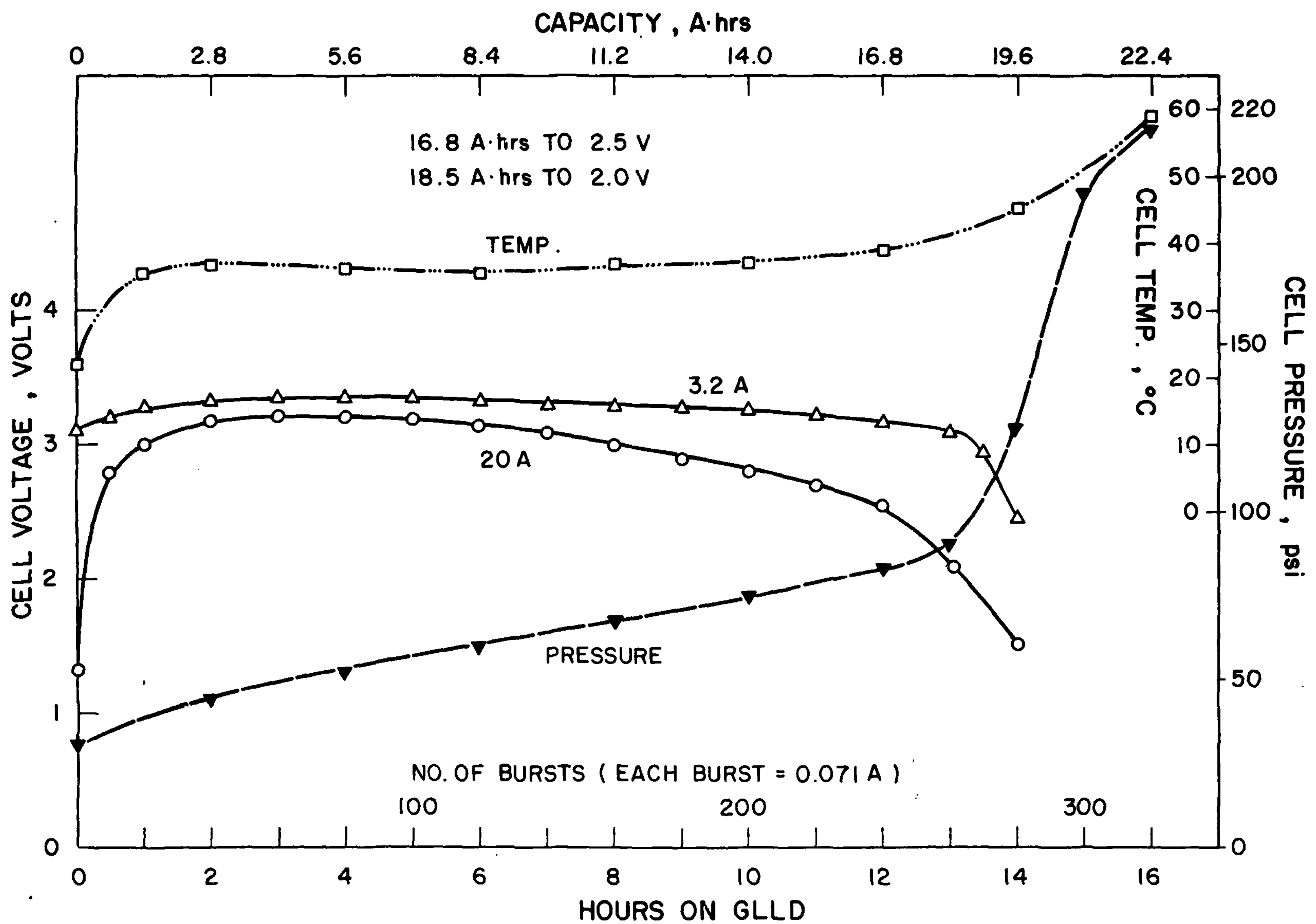

Fig. 16. Performance of a flat cell on GLLD test at room temperature after two days at 72°C and two days at 50°C

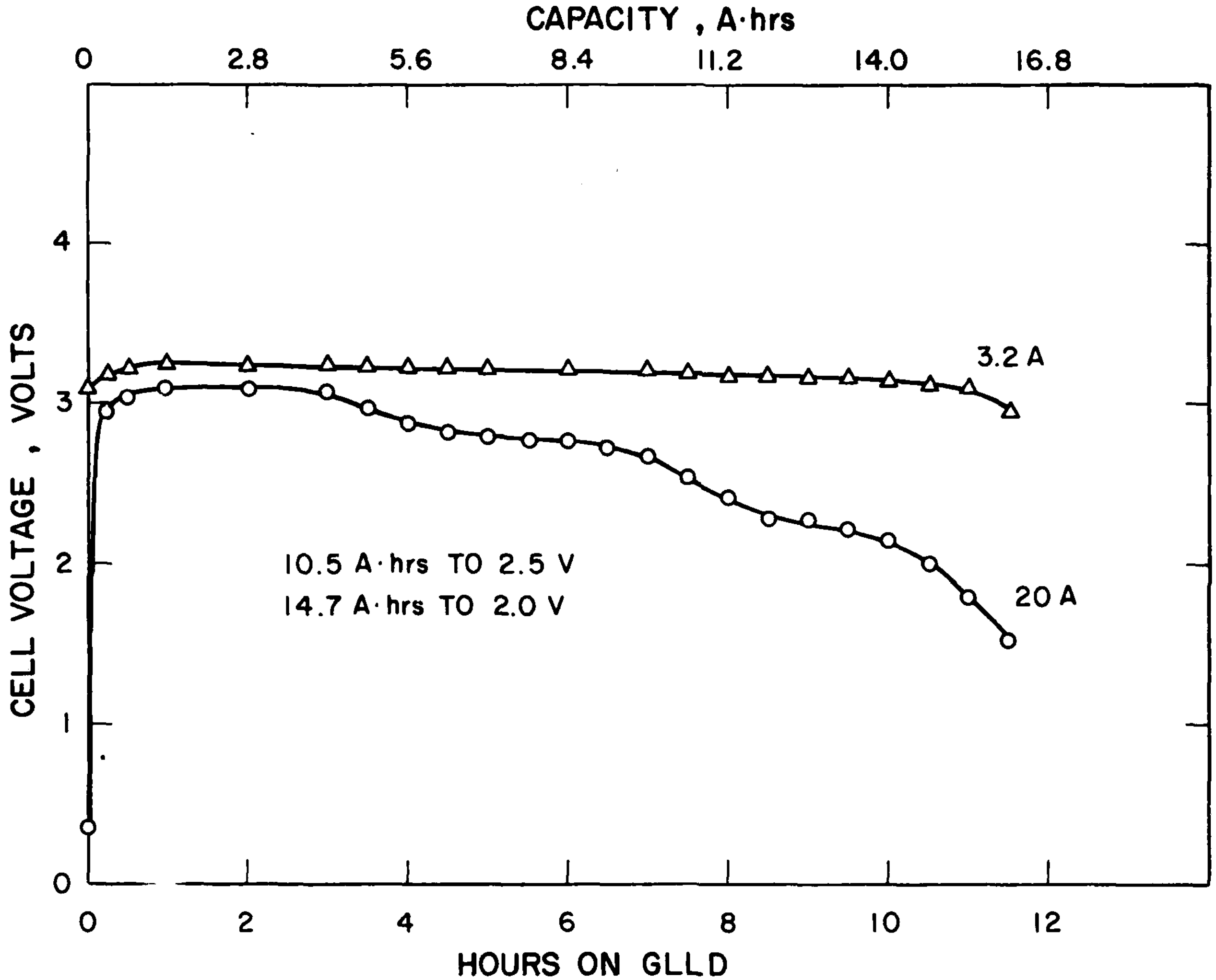

Fig. 17. Performance of a flat cell with cathode additive 1 on the GLLD test at room temperature after 2 days at 72°C and 3-1/2 days at room temperature

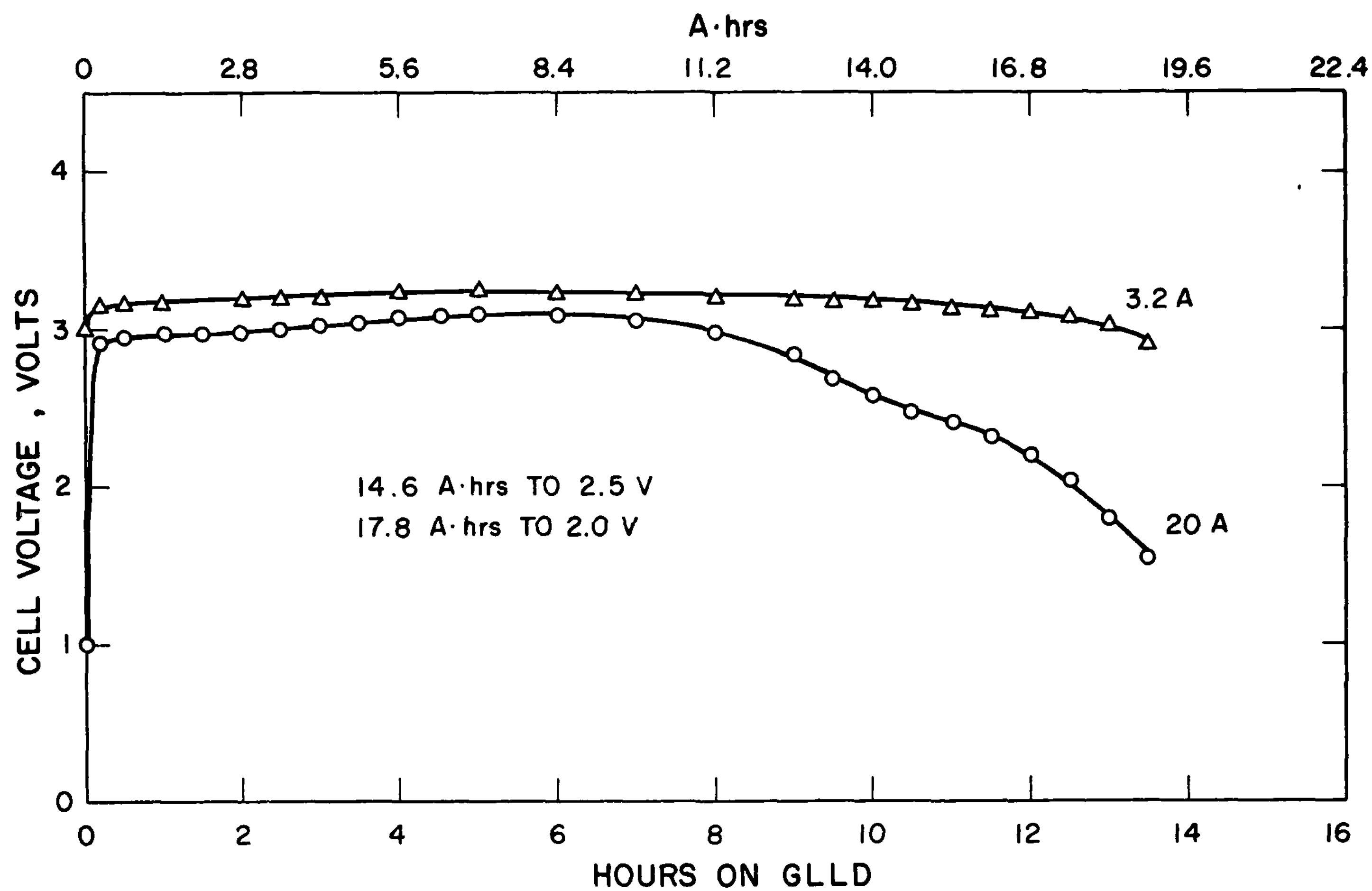

Fig. 18. Performance of a cell with vacuum dried cathodes on the GLLD test at room temperature after 1 day at 72°C and 3-1/2 days at room temperature

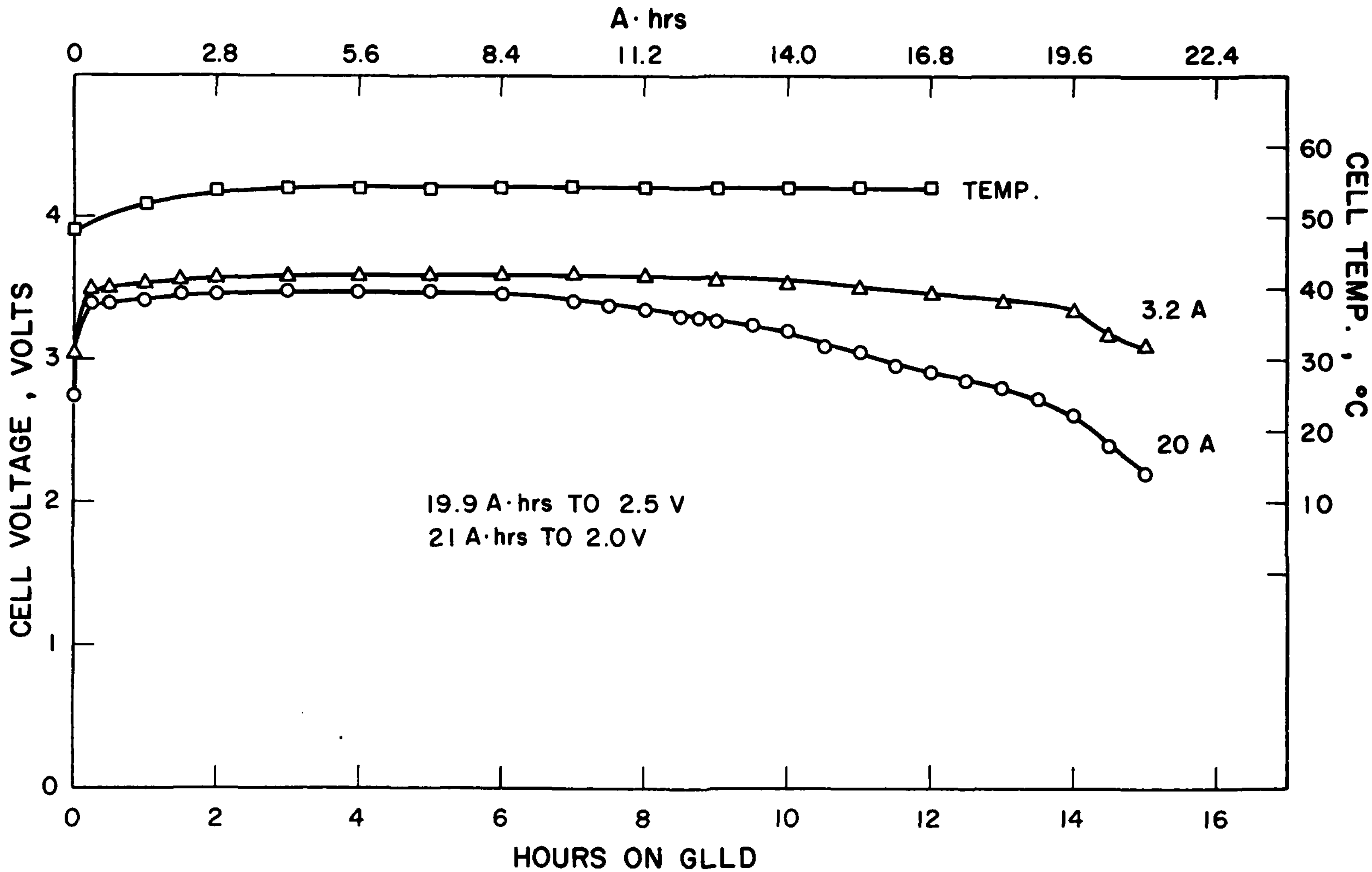

Fig. 19. Performance of a flat cell tested on the GLLD test at 48°C after three weeks at room temperature

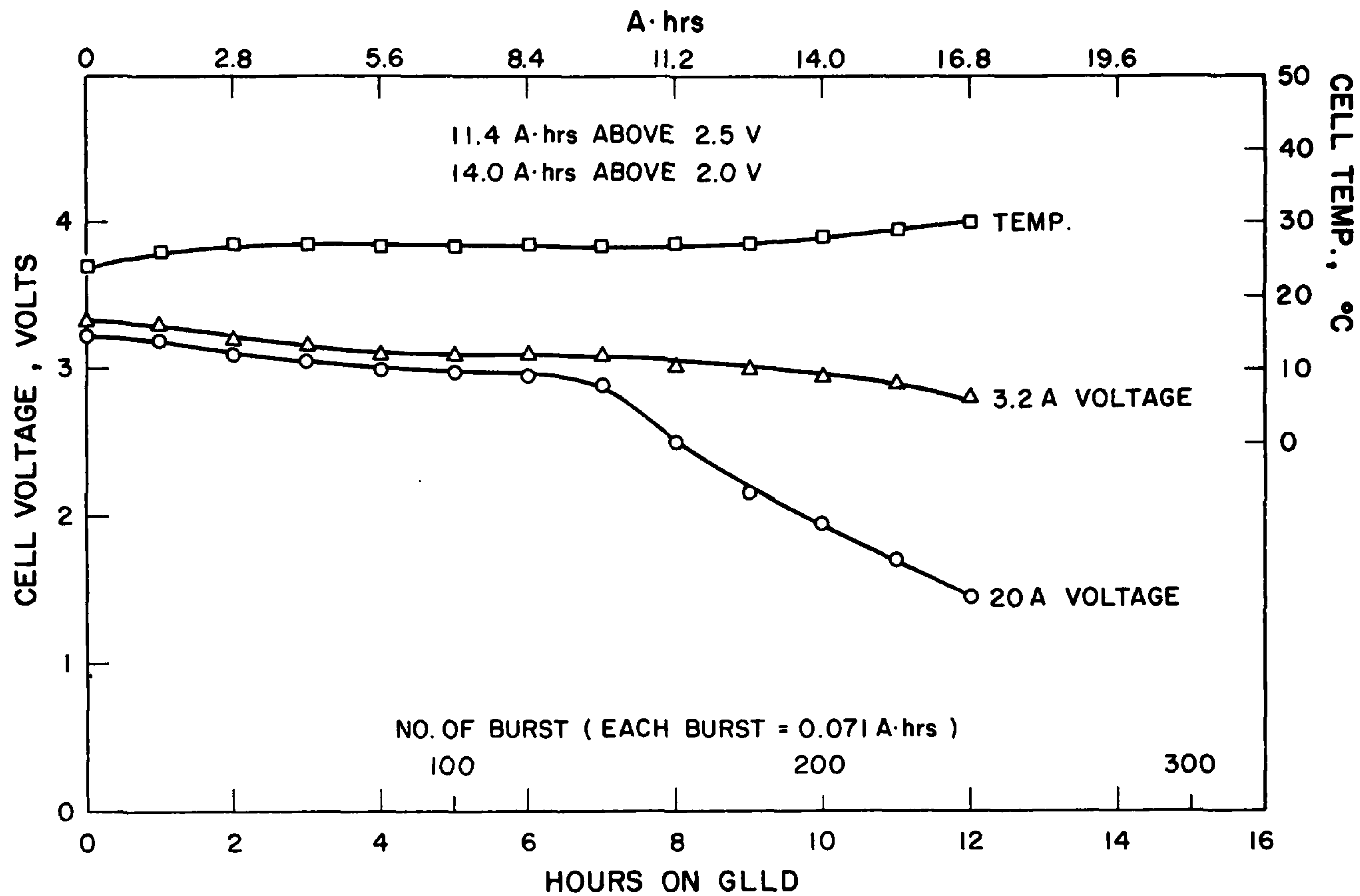

Fig. 20. Performance of a fresh flat cell with 1 M $LiAlCl_4$ at room temperature on the GLLD·test

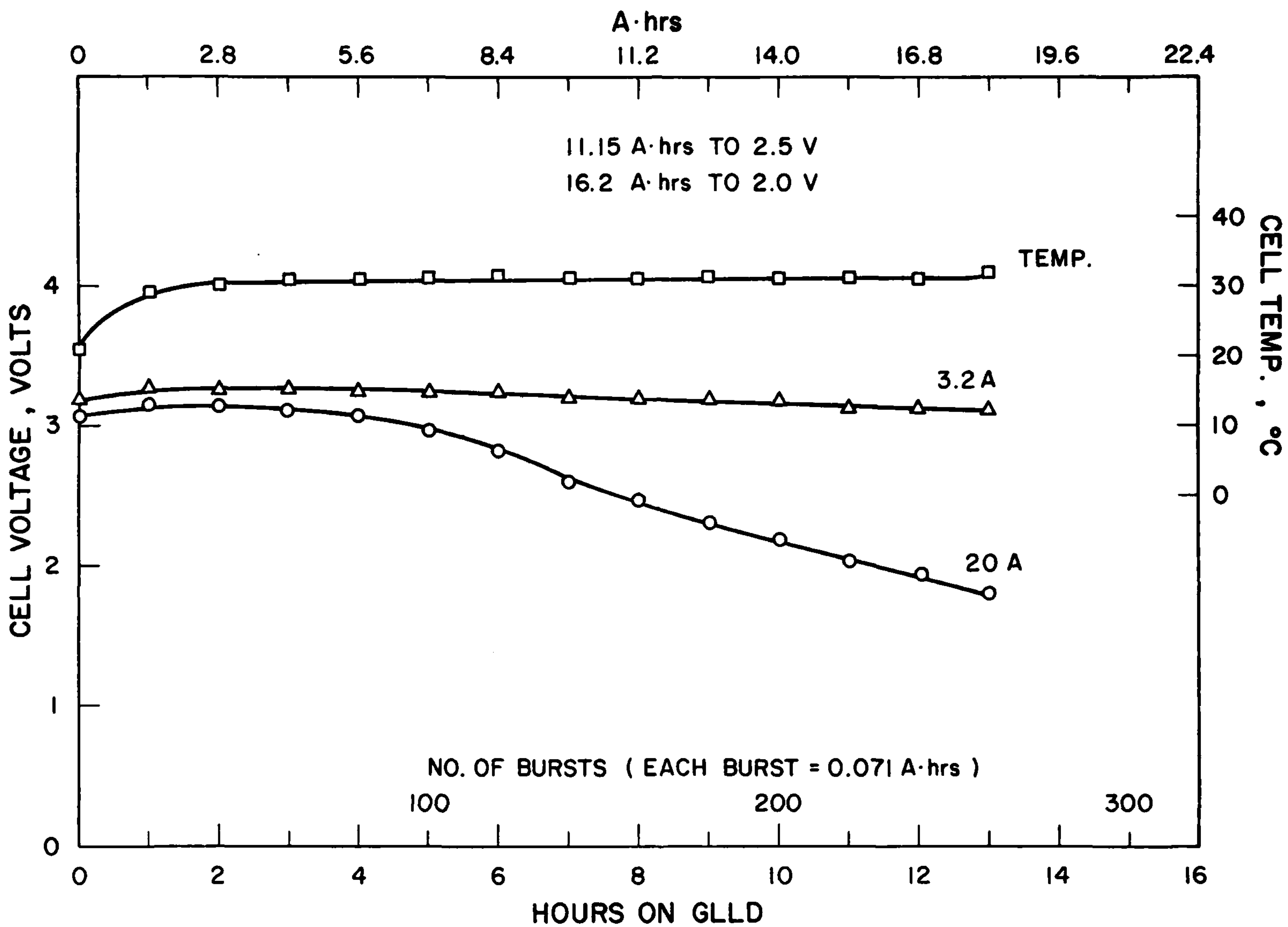

Fig. 21. Performance of a flat cell with 1 M $LiAlCl_4$ on the GLLD test at room temperature after two weeks at room temperature

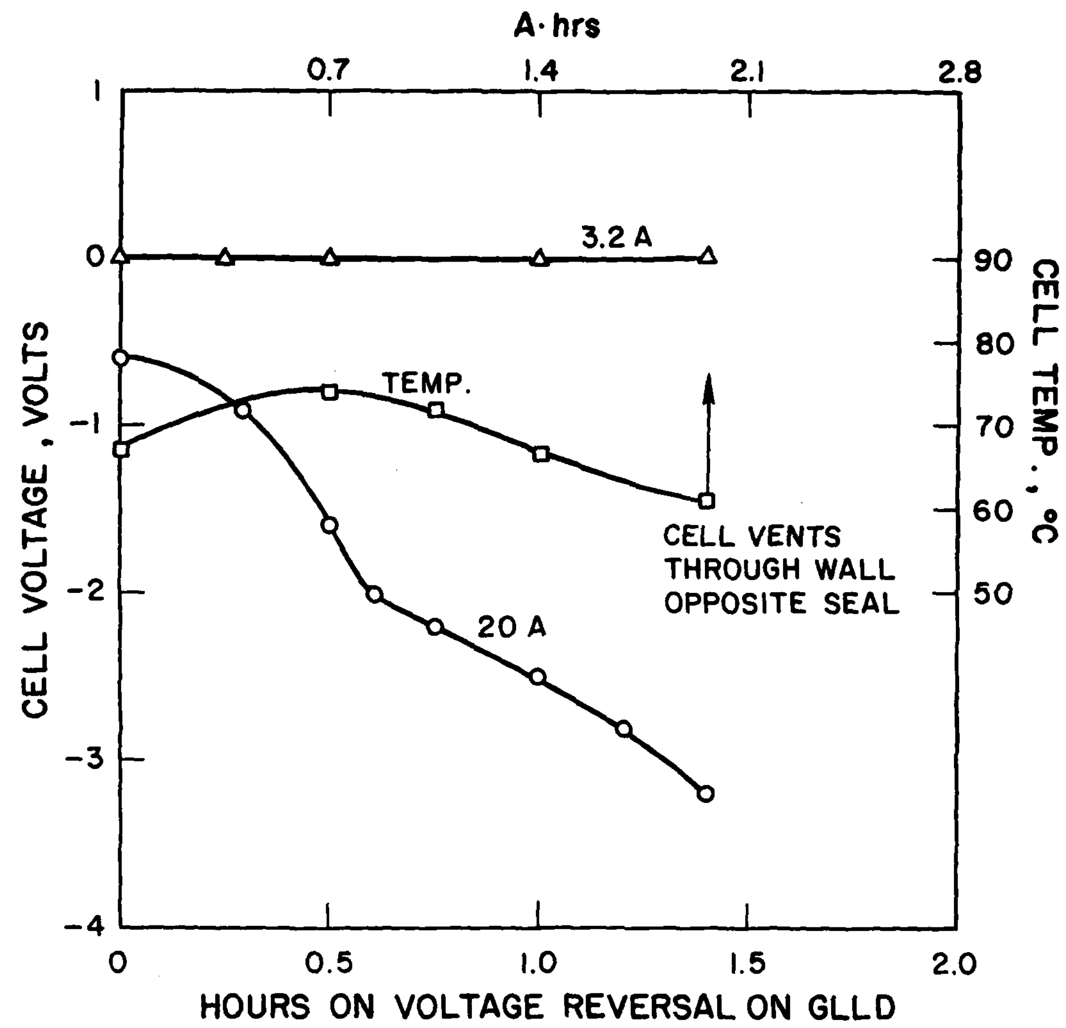

Fig. 22. Behavior of a flat cell during voltage reversat at 3.2A and 20A on the GLLD cycle

Fig. 23. Photograph of the vented flat cell with a fresh flat cell.

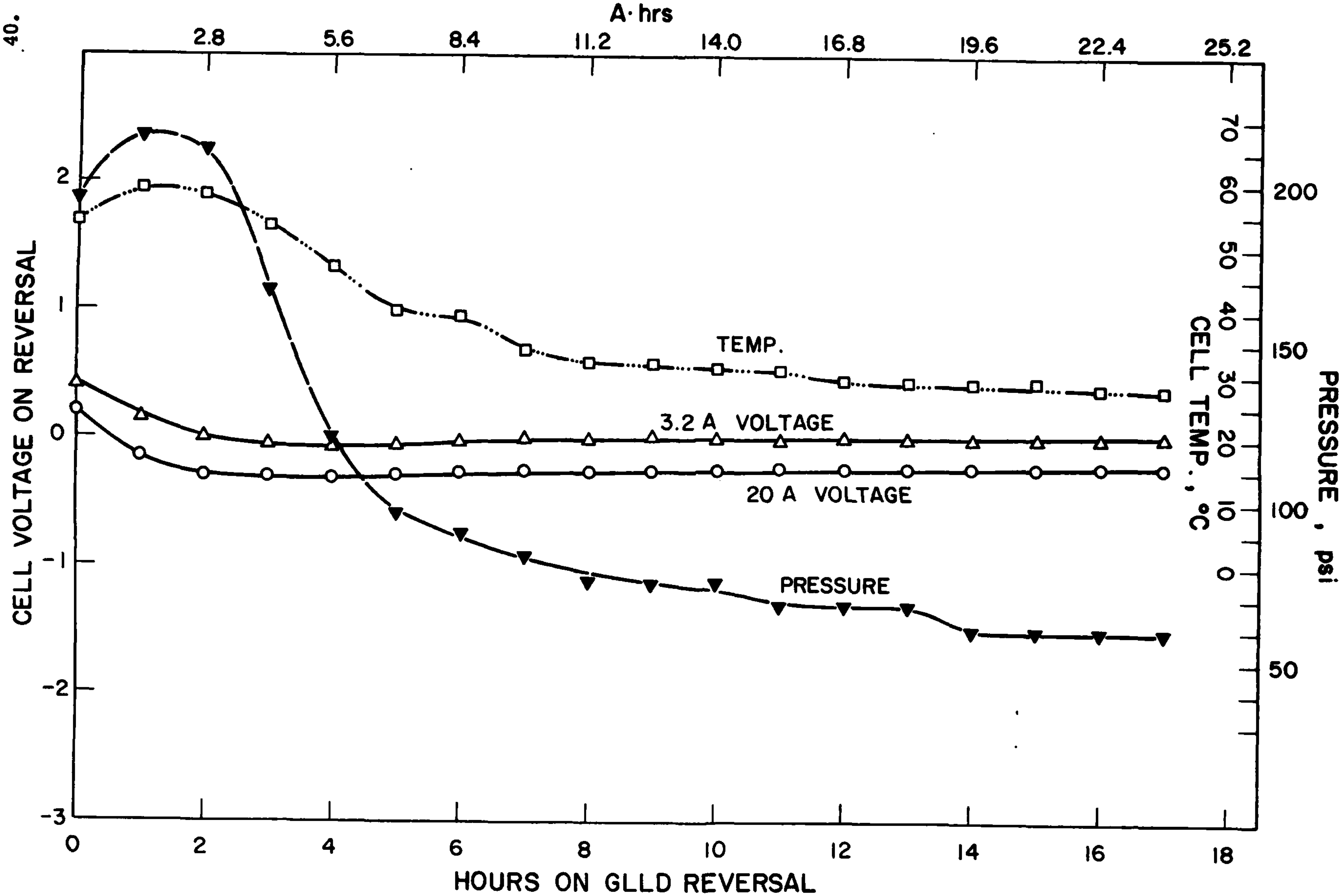

Fig. 24. Performance of a lithium excess flat cell during voltage reversal at the GLLD loads of 3.2A and 20A

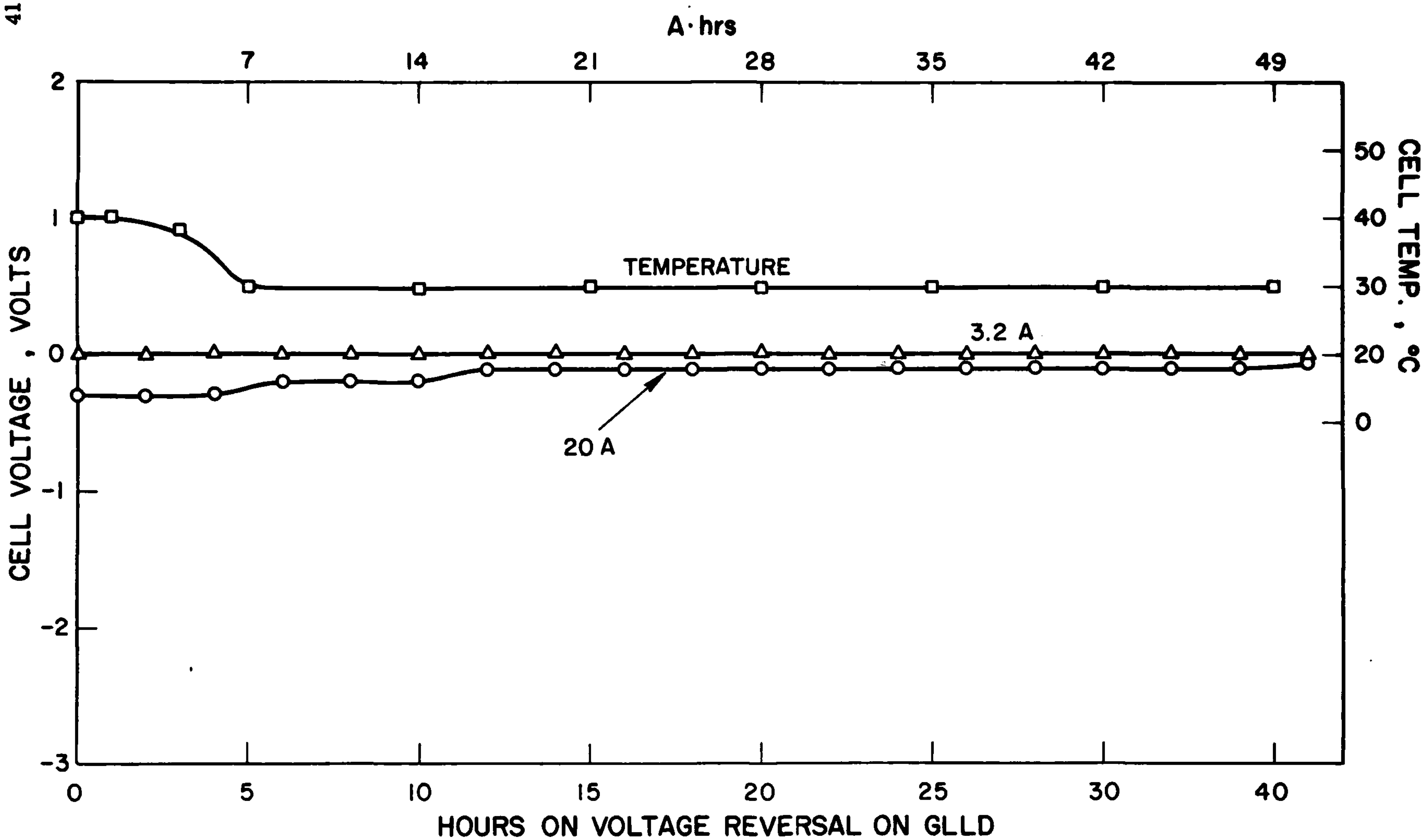

Fig. 25. Performance of a lithium excess flat cell during voltage reversal at the GLLD loads of 3.2A and 20A

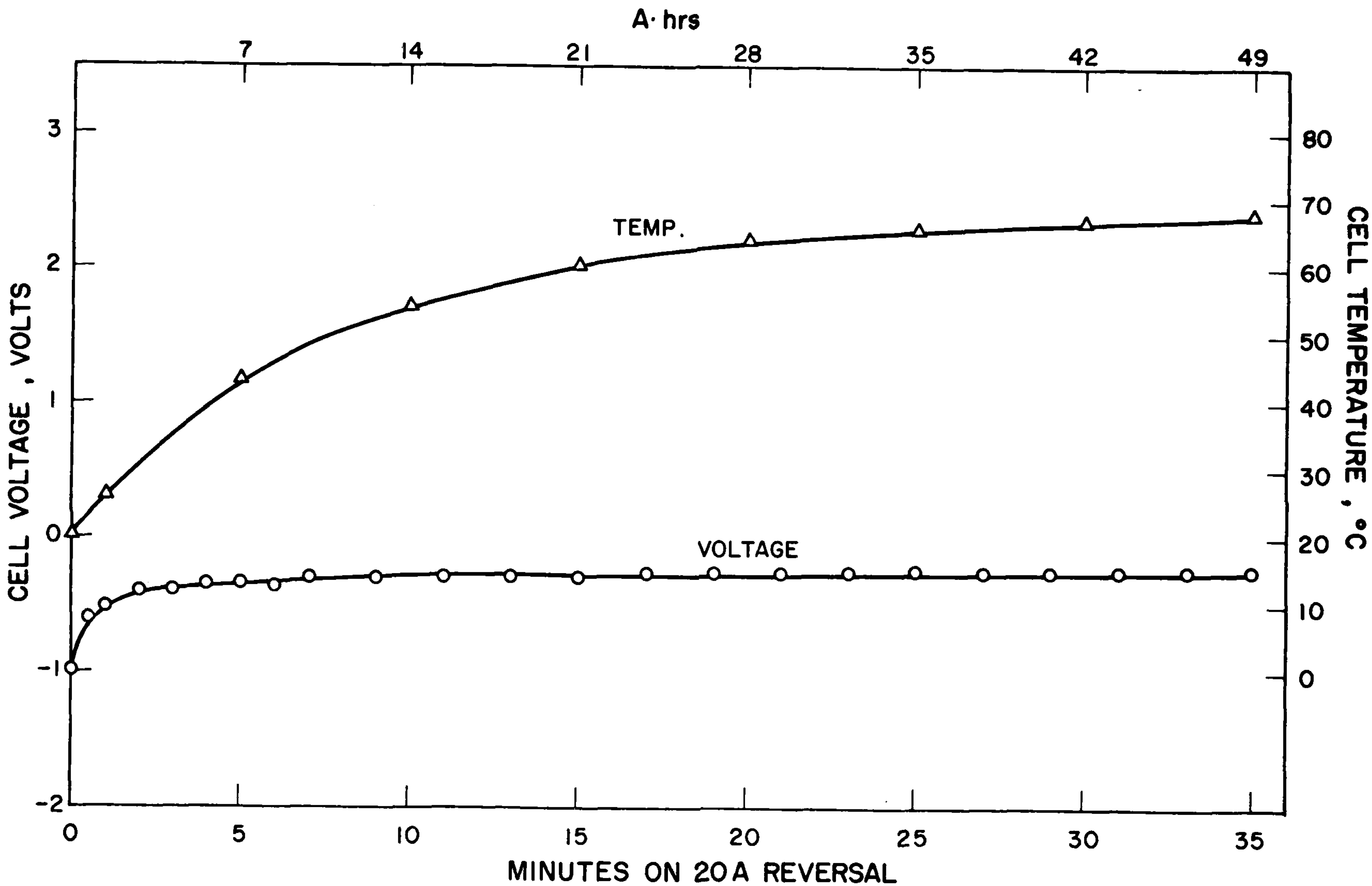

Fig. 26. Performance of a lithium excess flat cell on voltage reversal at 20A.

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